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**EVALUATE AND CHARACTERIZE MECHANISMS  
CONTROLLING TRANSPORT, FATE AND  
EFFECTS OF ARMY SMOKES  
IN AN AEROSOL WIND TUNNEL****Transport, Transformations, Fate and  
Terrestrial Ecological Effects of  
Fcg Oil Obscurant Smokes****Final Report**

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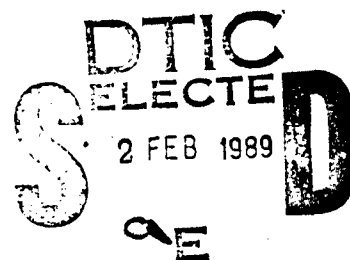
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**JANUARY 1989**

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<p>The terrestrial transport, chemical fate, and ecological effects of fog oil (FO) smoke obscurants were evaluated under controlled wind tunnel conditions. The primary objectives of this research program are to characterize and assess the impacts of smoke and obscurants on: 1) natural vegetation characteristic of U.S. Army training sites in the United States; 2) physical and chemical properties of soils representative of these training sites; and 3) soil microbiological and invertebrate communities. Impacts and dose/responses were evaluated based on an exposure scenario, including exposure duration, exposure rate, and sequential cumulative dosing. Key to understanding the environmental impacts of fog oil smoke/obscurants is establishing the importance of environmental parameters such as relative humidity and wind speed on airborne aerosol characteristics and deposition to receptor surfaces. Direct and indirect biotic effects were evaluated using five plant species and three soil types.</p> <p>(continued on reverse)</p>					
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Fog oil aerosols were generated in a controlled atmosphere wind tunnel by vaporization and condensation of SGF-22 fog oil under controlled conditions. The aerosol was characterized and used to expose plant, soil, and other test systems. Particle sizes of airborne fog oil ranged from 1.6 to 3.1  $\mu\text{m}$ , and the composition of the aerosol appeared to not be affected by relative humidity over a range of 20 to 91%.

Based on a deposited dose of 100 to 500  $\mu\text{g FO}/\text{cm}^2$ , equivalent to 2- to 8-hr exposure to smokes at 900  $\text{mg}/\text{m}^3$  air, plant toxicity responses are judged moderate. Relative humidity has no dramatic effect on the quality or intensity of damage. Repetitive dosing at 2- to 3-day intervals resulted in substantially less damage than indicated by the total delivered dose. This amelioration in effects results from the rapid loss by volatilization of fog oil from foliar surfaces. Residual effects, namely those that result from foliar absorption of smoke constituents that are transferred to below ground plant tissues, are apparent in several of the test series. Grass grown on Burbank soil was less affected than that grown on Maxey Flats soil. In no case was seed germination affected.

Fog oil enhanced the microbial activities in most of the metabolic parameters evaluated. A cumulative dose of fog oil exposure stimulated soil respiration slightly and increased nitro- bacter population in Palouse soil, and greatly increased soil enzyme activity in both Palouse and Burbank soil.

Earthworm bioassays indicated no adverse effect of fog oil with exposures up to 800  $\mu\text{g}/\text{cm}^2$  soil. In vitro studies, where fog oil was uniformly amended to soil, showed earth- worm survival to be 100% until an exposure of ~3600  $\mu\text{g}/\text{cm}^2$  (a soil concentration of 285  $\mu\text{g FO}/\text{g}$ ) was reached.

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## EXECUTIVE SUMMARY

Effective training scenarios for our armed forces require that troop maneuvers simulate, as closely as possible, the conditions most likely to be encountered under live combat situations (e.g., hardware, weapons fire, terrain, weather, vegetation, and smoke concentrations). Within the framework of the training operations, the U.S. Army has a regulatory responsibility to ensure that the use of smokes and obscurants does not adversely affect the health of local residents or the environment, both on and near the training sites. The environments of these training centers range from high deserts to semitropical forests, thus complicating this responsibility. The Health Effects Research Division of the U.S. Army Biomedical Research and Development Laboratory (USABRDL) has been assigned the responsibility of determining the potential environmental effects associated with the use of smokes and obscurants in training and testing.

As part of USABRDL's planned program in response to this concern, this project was implemented to evaluate the formation, transport, chemical transformations, deposition and the terrestrial ecological effects of smokes and obscurants currently used in training throughout the United States. Research related to smoke and obscurant testing employed a special recirculating wind tunnel that ensures containment of the smoke and permits simulation of a variety of environmental conditions (i.e., varying wind speeds, relative humidities, temperatures, and lighting conditions). The research described is similar to that performed with red phosphorus-butyl rubber and white phosphorus smokes (Van Voris et al. 1987).

Within the framework of the experimental design, our first objective was to evaluate the influence of two primary environmental variables, relative humidity (20%, 60%, 90%, and simulated rain) and wind speed (0.90 to 4.5 m/s, or 2 to 10 mph), on the ecological effects induced by these smokes. Our second objective was to characterize the physical and chemical properties of fog oil smokes. USABRDL will use this information in predicting dose associated with human health risk assessment models and for future assessments of smoke and obscurants effects on wildlife and domestic animals.

Environmental wind tunnels provide a method for the dynamic exposure of environmental components, such as plants and soils, and subsequent elucidation of the fate and effects of obscurant smokes. This approach allows for the simulation of a number of environmental variables affecting the physical and chemical nature of smoke aerosols. In the present studies, fog oil smokes were generated at elevated temperatures and reduced oxygen to simulate nominal field generation methods, and introduced into the air stream of the

recirculating tunnel, remote from the test section, to simulate aged aerosols that would be deposited 1500 m from the generator. Several environmental parameters were investigated, including exposure duration, relative humidity, wind speed, rainout during exposure and post-exposure simulated rainfall. Aerosols were continually monitored for concentration and size distribution to permit intercomparisons from test to test.

Several plant species and soil types were investigated based on dose response, intensity, and recovery. Plants were selected to be representative of native species found at regional training facilities. Investigations centered on elucidation of these physical parameters and processes affecting environmental performance resulting from recurrent use of obscurant smokes. Environmental components evaluated included foliar contact toxicity, indirect effects of soil contamination on plant growth, effects of soil-deposited smoke on soil microbial enzyme activity, and effects on earthworms. In all cases, responses were correlated with delivered dose/mass loading and not airborne smoke concentration.

Overall, results for fog oil smokes indicate a lower damage intensity than observed for phosphorus smokes resulting from foliar contact for either 8 hr or following repetitive dosing. Indirect soil/plant effects were marginal in most instances, and are not expected to be persistent. Soil microbial processes important in mineral cycling were not adversely impacted.

These studies were designed to enable prediction of environmental damage under a variety of field conditions. The versatility of these data to meet this use relies on measurements of dose/response relationships based on mass loading, and characterization of aerosol parameters allowing calculation of deposition velocities for specific receptor surfaces under specific environmental variables. For example, the length of time that a smoke test could be conducted without adversely affecting a specific plant species located 8 km downwind could easily be calculated based on the air concentration at that point, the deposition velocity for that canopy type, and wind speed. It is this predictive approach based on precise laboratory or field data that will be most useful in the future.

## FOREWORD

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## 1.0 INTRODUCTION

The U.S. Army has deployed a number of smokes and obscurants to visually mask the movement of troops and vehicles during combat. Effective training scenarios for our armed forces require that troop maneuvers simulate, as closely as possible, the conditions most likely to be encountered under live combat situations (e.g., hardware, weapons fire, terrain, weather, vegetation, and smoke concentrations). Within the framework of the training operations, the Army has a regulatory responsibility to ensure that the use of smokes and obscurants does not adversely affect the health of local residents or the environment, both on and near the training sites. The environments of these training centers range from high deserts to semitropical forests, thus complicating this responsibility.

The Health Effects Research Division of the U.S. Army Biomedical Research and Development Laboratory (USABRDL) has been assigned the responsibility of determining the potential environmental effects associated with the use of smokes and obscurants in training and testing. As part of USABRDL's planned program in response to this concern, the U.S. Department of Energy's (DOE's) Pacific Northwest Laboratory (PNL) was assigned to evaluate the transport, the chemical transformation, and the terrestrial ecological effects of several of the smokes currently used in training throughout the United States. PNL was assigned this task for two reasons. First, smoke and obscurant testing could be conducted within a special recirculating wind tunnel that ensures containment of the smoke and enables researchers to simulate a variety of environmental conditions (i.e., varying wind speeds, relative humidities, temperatures and lighting conditions). Second, PNL researchers have an established expertise in evaluating the interactions of plants and soils with aerosols and gases under controlled environmental conditions.

The health and environmental effects of Army smokes and obscurants have been studied intensively over the past 30 years; these research efforts have recently been compiled and reviewed by Shinn et al. (1985). In general, research into the effects of obscurant smokes has concentrated on animal and aquatic toxicity, with relatively little effort being expended in understanding soil/plant or other ecological effects. The vast majority of these previous efforts used direct artificial dosing of organisms or aqueous amendments of suspected toxicants. While this may be appropriate and necessary in many instances, it may not be appropriate in developing an understanding of the potential impact of the recurrent use of obscurant smokes at heavily used training sites. Artificial dosing is questionable because there is no established correlation between airborne smoke concentration, deposition on soils and plants (duration and physical parameters affecting deposition), and the ultimate effect, environmental deterioration.



Research into the phytotoxicity of oils of various types dates back over 100 years. The first modern reviews of the plant effects of oils and their components were by Crafts and Rieber (1948), Currier (1951), and Currier and Peoples (1954). They described the herbicidal properties of various types of oils and their components, and formed the basis of the modern day herbicide industry. More recently, Liss-Suter and Villaume (1978) and Muhly (1983) reviewed the available literature relating to the effects of diesel/fuel oils on vegetation. Although these reviews describe potential effects of fog oil obscurants on soils and plants, to our knowledge no studies relating directly to the environmental effects of fog oil smokes have been documented. Part of the problem is that fog oil obscurants are a nondescript class of feed materials based on diesel fuel oil or SGF-2 lubricating oil. However, with this limitation, a number of observations can be made.

The literature indicates that foliar sprays of lubricating oils are less phytotoxic than fuel oils or kerosene. Also, the composition of oils influences their toxicity. Oils containing cycloparaffin have been shown to be more toxic than those containing aromatic hydrocarbons, and oils containing paraffin are least toxic to trees (Ziegler 1939; Felts and Bromely 1936; Riedhart 1961). Fuel oil (No.2) applied to a silt loam, sandy loam, and black clay loam, prior to planting with turnips and beans, caused the plants to grow only in the treated sandy loam (Raymond et al. 1976). Plants that grew were stunted and deformed, and the effect was not ameliorated after 12 months of study. However, the same authors showed that the soil-amended oils were degraded by microorganisms. Research has also shown that the photolysis of fuel oil constituents by light in the uv range could be an ameliorating aspect in environmental situations.

On the whole, little definitive work has been done with respect to the ecological effects of fog oil. However, based on the literature a number of research needs can be proposed. These include: 1) dose/ effect responses for plants (direct and indirect), soils, and microbial communities; 2) the influence of photolysis processes on fog oil decomposition, particularly on foliar and soil surfaces; and 3) a need to conduct detailed chemical characterization of feed materials, aerosols, and deposited materials to place any dose/response into perspective.

Within the framework of the experimental design, our first objective was to evaluate the influence of two primary environmental variables, relative humidity (20%, 60%, 90%, and simulated rain) and wind speed (0.90 to 4.5 m/s or 2 to 10 mph), on the ecological effects induced by these smokes. Our second objective was to characterize the physical and chemical properties of fog oil smokes. USAE RDL will use this information in predicting dose associated with human health risk assessment models and for future assessments of smoke and obscurant effects on wildlife and domestic animals.

This report presents detailed results associated with the formation, transport, atmospheric transformation, deposition, and terrestrial ecological effects of fog oil smokes. The research described is similar in nature to that performed with red phosphorus-butyl rubber and white phosphorus smokes (Van Voris et al. 1987). The effects of aerosolized fog oil on three primary ecosystem components were evaluated:

- natural terrestrial vegetation characteristic of U.S. Army training sites in the United States,
- physical and chemical properties of soils at those sites, and
- soil microbiological and soil invertebrate communities.

## 2.0 MATERIALS AND METHODS

All smokes testing was conducted at the Aerosol Research Facility at Pacific Northwest Laboratory (PNL). This facility (Figure 2.1), which is located on the U.S. Department of Energy's (DOE) Hanford Site in southeastern Washington, contains an environmental wind tunnel suitable for testing obscurant smoke under a wide variety of environmental conditions. The facility and supporting laboratories are used for research involving generation, transport, deposition, and characterization of aerosols and gases in complex atmospheric environments. A more detailed description of the wind tunnel is provided in Section 2.2 and additional information can be found in Van Voris et al. (1987), and Ligothke et al. (1986).

### 2.1 TEST MATERIALS

Test materials were selected to represent actual field conditions. Fog oil was obtained from DOD stocks used for training activities. Plants and soils were representative of training sites located in both the eastern and western portions of the United States.

#### 2.1.1 Chemical Characteristics of Fog Oil

The fog oil employed in these studies was SGF-2 oil. Although similar to No. 10 motor oil without additives, SGF-2 fog oil contains many hydrocarbon compounds. Few of these are present in quantities greater than 0.1%. The fog oil used in all tests was from a single 55-gal barrel designated: SGF-2-3, Fog Oil, MIL-F 12070B, Type SGF-2, 9150-00-261-7895, Lot #1, DLA Goo-83-C-1284, Date MFD 7-83. The fog oil was stored under a nitrogen atmosphere and at low temperature to prevent oxidation and the possible formation of sludge. No discoloration or sludge formation was observed over the duration of the experiments. Fog oil aerosols were generated only from the SGF-2-3 barrel.

### 2.2 WIND TUNNEL EXPOSURE FACILITY

A vital aspect of the project was simulation of natural field conditions. Conditions found in the field, such as wind speed, relative humidity, sunlight, and temperature, can significantly alter the physical and chemical characteristics of obscurant smokes such as fog oil. In addition, field conditions can alter the way these compounds interact with the environment. A special wind tunnel facility available at PNL simulated the natural environmental conditions that occur during training activities with fog oil obscurants. Figure 2.1 shows the facility and wind tunnel.

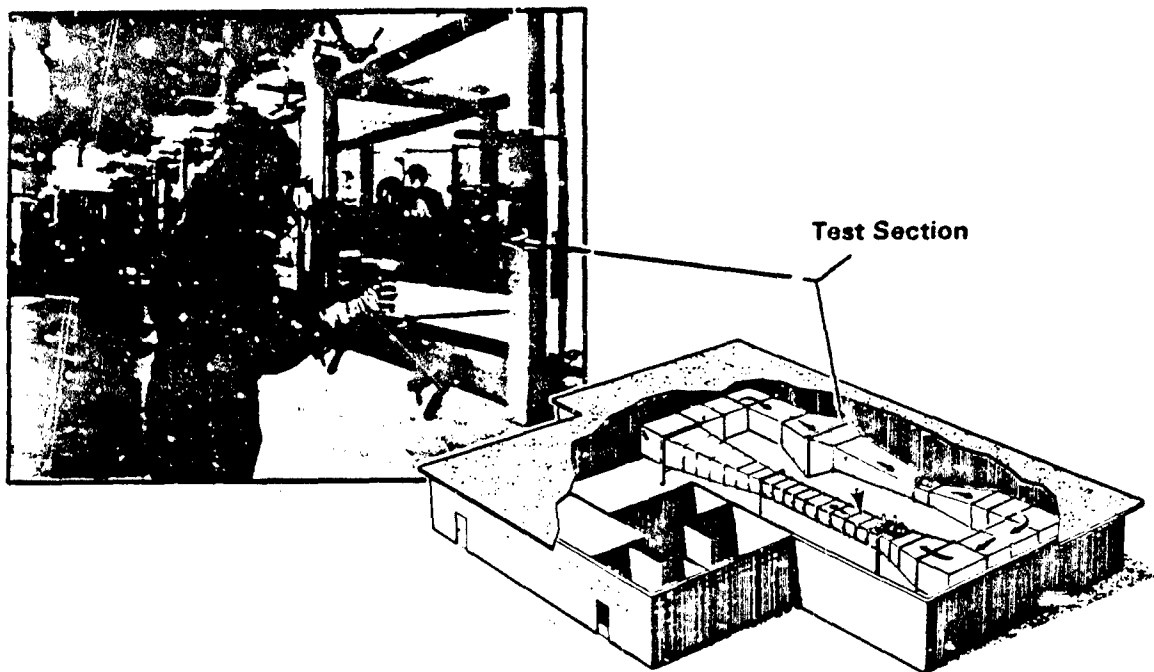


FIGURE 2.1. PACIFIC NORTHWEST LABORATORY ENVIRONMENTAL WIND TUNNEL FACILITY

#### 2.2.1 Wind Tunnel Design and Configuration

The environmental wind tunnel located within the 70-m<sup>3</sup> Aerosol Research Facility is constructed of stainless steel, except for the clear Lexan® walls and ceiling of the test section. Wind speed, temperature, humidity, and lighting are controlled within the system to provide natural environments for testing. Most laboratory instrumentation is connected to a computer control and data acquisition system to improve testing and subsequent data analysis procedures. The wind tunnel may be operated as a continuous-loop system, as was done to maintain stable aerosols of fog oil obscurant, or may be operated as a single-pass wind tunnel by insertion of a bank of high-efficiency particulate air (HEPA) filters in the return section. Toxic and hazardous materials may be used safely within the laboratory and wind tunnel; the facility was designed with special back-up power systems and chemical containment capabilities, and the wind tunnel is operated at negative air pressure to contain airborne materials. All effluent exhausted from the wind tunnel or facility is cleaned in scrubbers and filters prior to release.

Fog oil obscurant aerosols were produced for the wind tunnel using a laboratory-scale generator representative of actual field generators (Section 2.32). Concentrations of the obscurant were generally maintained in the 100 to 1000 mg/m<sup>3</sup> range to replicate actual conditions during Army field training activities. Fog oil aerosols were characterized using conventional and state-of-the-art instruments. Laser transmissometers were used to measure the mass concentration of fog oil aerosols within the wind tunnel, and cascade impactors were used to measure particle size distribution. The transmissometers were mounted next to the test section and provided in situ measurement of aerosol characteristics, thus avoiding the need to place a sampling probe upwind of deposition subjects (primarily plants). Use of such a probe would have disturbed the air flow and particle deposition characteristics. Cascade impactors were selected to provide measurements of particle size distribution because of their suitability over the range of droplet sizes formed in the fog oil aerosol generator.

#### 2.2.2 Description of Wind Tunnel Test Section

The primary test section of the wind tunnel was used for all exposures of plants and soils to fog oil aerosols. This test section is 6.1 m long and 0.6 m wide (Figure 2.2). One 2.0-m-wide and two 1.5-m-wide test sections are also available for use. Wind speed is controlled to 30 m/s (~70 mph) in the primary test section. Lighting suitable for sustaining plant respiration is provided by 400 W metal halide lamps. The inlet to the test section is shaped to provide a uniform flow of air with minimum wall turbulence; velocities are uniform within 3% over the width of the test section. A false floor, provided over the length of the test section, was used to contain the pots of plants exposed to fog oil aerosols. Using movable internal baffles, the test section can be isolated from the wind tunnel and purged of aerosol prior to or following tests to facilitate exchange of plants and other test subjects.

### 2.3 EXPOSURE CONDITIONS

The exposure environment was controlled. Both wind speed and relative humidity were varied as test parameters. Concentration of fog oil aerosol and time of exposure were also controlled to provide test conditions. Temperature was not a test parameter for fog oil tests. The environmental and aerosol conditions occurring during tests were monitored and recorded using the computer system and other devices such as isokinetic samplers and cascade impactors. After setting the test environment, fog oil was generated and introduced to the wind tunnel. Fog oil aerosol generation was continuous during all tests, providing a stable aerosol over periods of several hours.

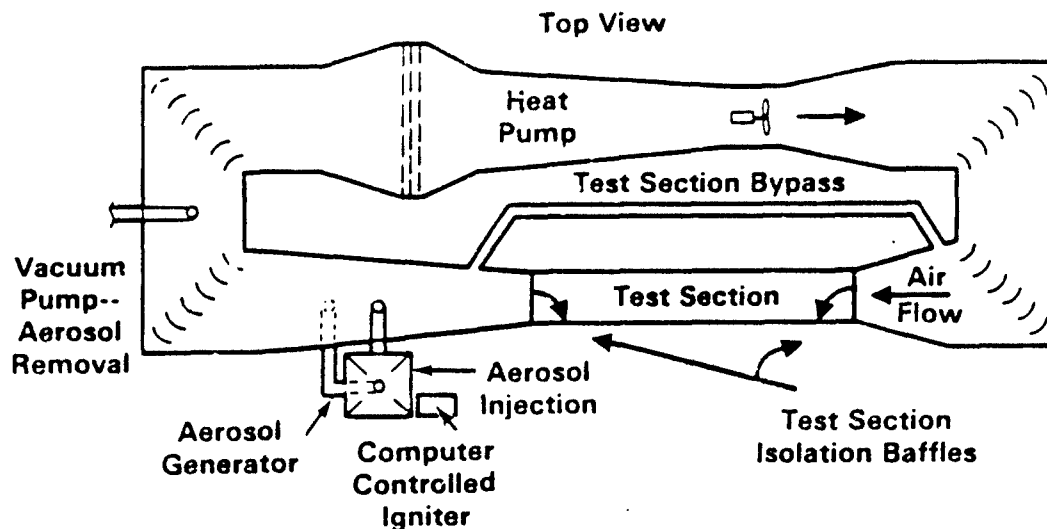


FIGURE 2.2. WIND TUNNEL AND FOG OIL AEROSOL GENERATION SYSTEM, INCLUDING TEST SECTION BYPASS

### 2.3.1 Exposure Environment

Environmental parameters in the wind tunnel were controlled to closely match those existing in the field. Air temperature was constant between 20° to 23°C during most tests. The relative humidity of the wind tunnel atmosphere was controlled and ranged from 20 to 90% depending on specific test requirements; water vapor was added to the system to maintain the higher humidities. Tests were performed at wind speeds of 0.9, 1.8, 2.7, and 4.5 m/s (2 to 10 mph).

The humidity of the wind tunnel atmosphere was typically measured during each test using a General Eastern Model 1500 Hygrocomputer. Samples were drawn from the wind tunnel through a 30-cm-long cylindrical Teflon® filter. The filter was shielded from impaction of fog oil droplets; however, fumes from the lighter organic compounds present in the fog oil aerosol were passed through the filter and deposited to the chilled mirror sensor of the hygrocomputer. The sensor therefore required periodic cleaning and was only used at regular intervals during tests. The hygrocomputer was also used to measure wind tunnel temperature, and was calibrated against a precision controlled-draft sling psychrometer.

The mean, or average, wind speed approaching the test subjects in the wind tunnel test section was measured using a Thermal Systems Incorporated (TSI) hot-film probe Model No. 1366 connected to a TSI Model No. 1054A anemometer. This device was calibrated by comparison to a pitot-static probe; a laboratory standard for air velocity measurement. The pitot-static tube was positioned on the center line in the wind tunnel test section and connected to a Dwyer Model No. 1430 micromanometer. This procedure provided calibration of the hot-film probe at a location just upwind of the test section.

### 2.3.2 Fog Oil Generator Operation

Aerosols of vaporized and condensed fog oil were produced by pumping oil at steady rates from a reservoir to the smoke generator shown in Figure 2.3. Liquid fog oil was pumped onto the surface of an immersion heater, which was maintained at 600°C and contained within a 1-m-long, 2.5-cm-diameter stainless steel pipe. The immersion heater caused the oil to vaporize under controlled thermal conditions; this vapor was then carried in a mixture of nitrogen (96%) and air (4%) carrier gas through a region controlled at 300°C, into a buffer tank with a residence time of approximately 5 min, and into the wind tunnel. The oxygen content in the carrier gas was approximately 0.8%, a value that was determined to be typical of the oxygen content present in the exhaust of diesel engines.

The flow rate of oil into the generator was varied between 1 and 6 ml/min to produce concentrations required for exposures within the wind tunnel. The feed rate was adjusted periodically, based on the computer-monitored aerosol concentration, to maintain required concentrations. Freshly generated aerosols were mixed with air in the buffer tank to allow initial cooling and mixing to attain desired aerosol concentrations within the test section. Aerosols were passed from the buffer tank into the wind tunnel downwind of the test section (Figure 2.2), which allowed the fresh aerosol plume to mix completely and come to thermal equilibrium with the wind tunnel atmosphere prior to approaching the wind tunnel test section. No thermal stratification was observed and aerosol concentrations were uniform in the approach flow to the wind tunnel test section.

### 2.3.3 Test Procedures and Measured Conditions

Because physical and chemical characteristics of aerosols change as they age following generation by combustion, fog oil aerosols were introduced into the wind tunnel continuously and allowed to age during the exposure tests. Use of the dynamic exposure environment within the wind tunnel provided close representation of actual field conditions. Use of static test chambers was avoided because of the need to accurately reproduce fog oil

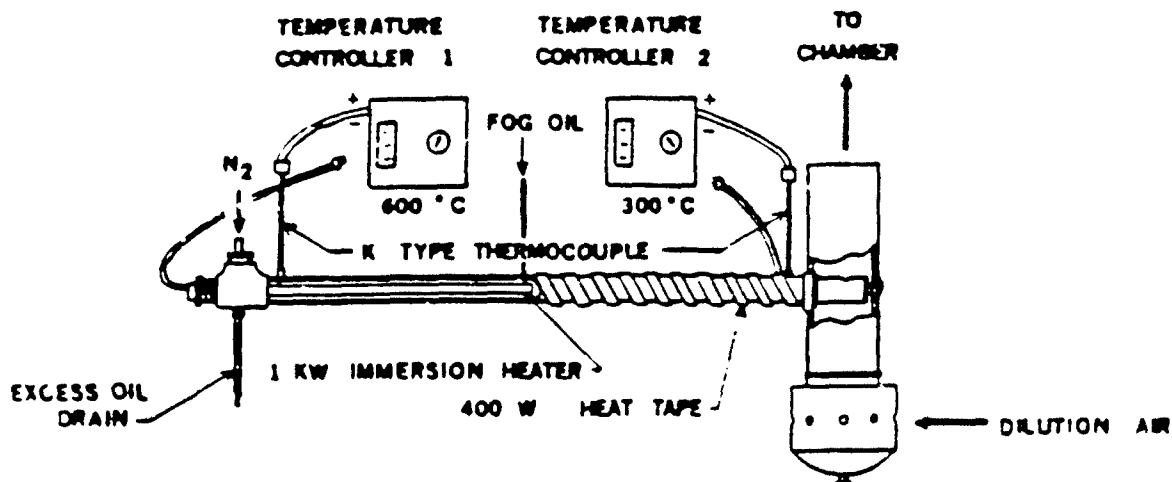


FIGURE 2.3. TEMPERATURE-CONTROLLED FOG OIL AEROSOL GENERATOR

deposition characteristics, which are strongly influenced by wind speed. To prevent unrealistic aging of the fog oil aerosols in the wind tunnel, a flow of carrier air was provided to the buffer tank to transport the aerosol into the wind tunnel, and an equivalent flow was drawn out of the wind tunnel. This transfer flow rate was approximately 25 cfm and resulted in a net loss of aerosol from the wind tunnel system of approximately 1% per minute. Aerosol losses by deposition to the test subjects and the surfaces of the wind tunnel accounted for an additional ~1% per minute. The fog aerosol was therefore a mixture of freshly generated and aged particles; this experimental laboratory approach was believed to provide accurate simulation of actual field conditions. Based on the residence time within the wind tunnel, the average age of the fog oil aerosol in the wind tunnel was estimated to be 41 min, or similar to that of a field-generated aerosol that had drifted approximately 2 km downwind under the influence of a slow [0.9 m/s (2 mph)] wind.

The duration of the exposure interval for each wind tunnel test was based on visual observation of the smoke density. Test start times were nearly instantaneous and thus easily estimated. The test section was bypassed prior to each test until a constant concentration of the aerosol was present in the wind tunnel, with the test section isolated and containing fresh air. The time required to attain steady state concentrations ranged from 20 to 30 min. At that time, the exposure was begun by allowing fog oil smoke to pass through the test section and closing the bypass loop (Figure 2.2). Aerosol generation continued until the test was finished, at which time the test section was again isolated and flushed with fresh air. Because approximately 5 min were required to flush the visible smoke from the test section at the end of



each test, the end of the exposure test was assigned to that time when the test section purge was half complete, which was typically 2 or 3 minutes following initiation of test section purging.

Test durations were typically 2, 4, 6, or 8 hr. Tests consisted of a single exposure to fog oil obscurant smoke. In addition to tests for instrument calibration or tests of the fog oil aerosol generator, four series of fog oil tests (FOT) were performed: range finding, relative humidity, wind speed, and cumulative dose. Conditions measured during tests are listed in Table 2.1. Aerosol mass concentrations typically ranged from 700 to 1000 mg/m<sup>3</sup> except during the 18 cumulative dose tests in which fog oil concentration was controlled at approximately 100 mg/m<sup>3</sup> (low-dose series) and 550 mg/m<sup>3</sup> (high-dose series). The range finding tests included exposures of 2-, 4-, 6-, and 8-hr durations. Four relative humidity tests were completed; the first three at 20%, 64%, and 91%, and the fourth at 61% with an intermittent precipitation event occurring during the second half of the test (during which time the wind tunnel relative humidity averaged 86%). Wind speed tests were performed at 0.91, 1.81, 2.70, and 4.54 m/s (~2 to ~10 mph). Two series of cumulative dose tests were performed simultaneously. In both series, test subjects were exposed to nine tests over a 3-wk period.

#### 2.4 SMOKE (AEROSOL) CHARACTERIZATION

Fog oil aerosols are produced in the laboratory and the field by vaporization of liquid fog oil at high temperatures and subsequent condensation of the vapors to form a droplet mist, or aerosol. Physical and chemical characteristics of the aerosol produced in the laboratory and wind tunnel were measured. The alteration of chemical form is not thought to be great; both the base liquid and the suspended droplets consist of many organic compounds. It is possible, however, that a lesser percentage of the lightest, most volatile, compounds are present in the liquid phase of the aerosol because of reduced potential for condensation.

In addition to the chemical composition of the obscurant aerosols, concentration and particle size distribution are important characteristics of the aerosol and affect the dose of fog oil and effects on the environment. The mass concentration of suspended droplets is the characteristic most directly linked to the bulk dose, or mass loading of fog oil onto environmental surfaces such as plants and soils. The particle size distribution of fog oil aerosols also influences deposition rates; large particles deposit more readily under the influence of wind speed and gravitational forces, small particles by diffusion. In addition, the location at which particles deposit is a function of their size.

**TABLE 2.1 ENVIRONMENTAL CONDITIONS, WIND SPEED, AND EXPOSURE DURATION FOR FOG OIL OBSCURANT TESTS**

Test	Date	Temp. (~C)	Relative Humidity (%)	Wind Speed (m/s)	Exposure Duration (min)
<b>Range Finding(a)</b>					
FOT-4-4	7/24/85	20.5	58	0.73	240
FOT-4-8	7/24/85	20.9	58	0.73	480
FOT-5-2	7/26/85	19.8	55	0.73	120
FOT-5-6	7/26/85	20.2	52	0.73	360
<b>Relative Humidity(a)</b>					
FOT-12	11/22/85	22.4	20	0.90	240
FOT-14	11/25/85	21.9	64	0.90	242
FOT-15	12/2/85	22.0	91	0.90	240
FOT-16(dry)	12/4/85	22.8	61	0.90	120
FOT-16(rain)	12/4/85	21.7	86	0.90	120
FOT-16(both)	12/4/85	22.3	74	0.90	240
<b>Wind Speed(a)</b>					
FOT-17	12/17/85	22.4	66	0.91	60
FOT-18	12/17/85	21.4	72 <sup>a</sup>	4.54	45
FOT-19	12/19/85	20.2	62	1.81	60
FOT-20	12/19/85	20.9	58	2.70	60
<b>Cumulative Dose(b)</b>					
FOT-22a	2/5/86	23.0	59	0.91	240
FOT-22b	2/6/86	22.3	61	0.90	240
FOT-23a	2/7/86	22.8	59	0.90	120
FOT-23b	2/7/86	22.5	60	0.89	120
FOT-24a	2/10/86	22.6	62	0.88	120
FOT-24b	2/10/86	22.5	58	0.84	180
FOT-25a	2/12/86	22.5	64	0.91	150
FOT-25b	2/12/86	22.4	60	0.90	120
FOT-26a	2/14/86	23.2	61	0.93	120
FOT-26b	2/14/86	23.1	56	0.86	120
FOT-27a	2/18/86	21.3	61	-0.9	120
FOT-27b	2/18/86	22.1	58	-0.9	121
FOT-28a	2/19/86	23.7	58	-0.9	120
FOT-28b	2/19/86	22.9	56	-0.9	110
FOT-29a	2/21/86	22.1	63	0.89	120
FOT-29b	2/21/86	22.3	60	0.91	120
FOT-30a	2/24/86	23.8	63	-0.9	120
FOT-30b	2/24/86	25.0	60	-0.9	120

(a) Aerosol mass concentrations ranged from 700 to 1000 mg/m<sup>3</sup>.

(b) Aerosol mass concentrations for low and high dose exposures were 100 to 550 mg/m<sup>3</sup>.

#### 2.4.1 Aerosol Mass Concentration

Aerosol mass per volume of air is an important characteristic of aerosols that must be measured during particle deposition studies. The mass concentration of suspended material is directly related to the amount of the material that eventually deposits on the ground, vegetation, and other surfaces, and is thus directly related to the effects that the deposited material may have on biotic systems. When aerosol mass concentration is compared to the mass loading on exposed surfaces, the rate at which particles deposit on a surface under specific environmental conditions, the particle deposition velocity, may be calculated. This provided a basis for both intercomparison of treatment effects and prediction estimates under field conditions. Several methods were routinely employed to obtain real-time and time-averaged estimates of aerosol mass concentration.

Isokinetic filter samples were taken periodically during each test to provide the primary method of measuring aerosol concentration in the wind tunnel. These samples were obtained at 15- to 30-min intervals by passing a known volume of aerosol through a 25-mm glass fiber filter. Sample volumes were measured using a calibrated dry gas meter. The mass of aerosol material collected on the filter divided by the volume of the sample provided a direct measure of aerosol mass concentration. It was necessary to sample the aerosol isokinetically because of the velocity of air flow within the wind tunnel and the inertia of the suspended fog oil particles. To test the aerosol, the filter substrate was placed in the wind tunnel in front of each sample and behind a sharp-edged sampling nozzle. The sample flow rate and the diameter of the sharp-edged nozzle were varied for the different wind speeds used during the exposure tests to keep the velocity of the sample within the sampling nozzle equal to the wind tunnel free-stream velocity. Significant deviations from isokinetic conditions would have biased the samples, and were avoided. Subisokinetic sampling can increase the sample collection of the larger particles in fog oil aerosols, and superisokinetic sampling can reduce the sampling collection of the larger particles because of their inertia. After each sample was obtained, the sample was weighed within two minutes and then extracted with isooctane for subsequent chemical analysis, or allowed to dry in the laboratory or in a desiccator for determination of the volatile fraction of the sample.

A secondary method of measuring aerosol mass concentration was performed to provide a continuous record of concentration during each test. Obscuration of a He-Ne laser beam (wavelength = 633 nm) was measured to provide a relative measure of aerosol mass concentration. The beam of the laser transmissometer was propagated horizontally across the wind tunnel test section just upwind of the test subjects. Transmitted laser intensities were compared to a reference measurement of output laser intensity typically at 45-sec intervals.

This system was modified after the range-finding tests and again prior to the cumulative dose test series. However, a new series of calibrations versus isokinetic filter samples was performed during most tests.

Laser transmissometer calibrations were performed and were found to be linearly related to aerosol mass concentration. Calibrations made during exposure tests having differing humidities did not show major deviations as was the case for similar measurements made with red phosphorus/butyl rubber and white phosphorus aerosols. This difference may be attributed to the much smaller contribution of liquid water to fog oil aerosols under humid conditions. Figure 2.4 shows the calibration results for tests FOT-12 through FOT-20, the wind speed and relative humidity tests. While minor ( $< 10\%$ ) deviations were observed from test to test, no major calibration shift was seen. Table 2.2 shows the linear calibration relationships determined for most fog oil tests.

#### 2.4.2 Particle Size Distribution

The size of particles that make up an aerosol often determine which forces, inertial or diffusive, control transport and deposition phenomena. The deposition velocity of particles to surfaces varies with the particle size; typically, particles with aerodynamic diameters between 0.1 and 1.0  $\mu\text{m}$  deposit less quickly than smaller or larger particles. This difference exists because even smaller particles are strongly affected by diffusive forces and larger particles by inertial forces. Aerosols observed in the field are polydisperse; they are made up of particles of many different diameters. The size distribution of such aerosols is often log normal and may thus be well characterized by a mean or median size and a standard deviation. Measuring the particle size distribution of an aerosol (the frequency of particle occurrence as a function of particle diameter) is important in describing an aerosol's physical characteristics. The particle size distribution of an aerosol may be based on particle number frequency, aerosol mass, or other parameters such as surface area or particle volume. The particle size distributions of the fog oil aerosols generated in this study were characterized by aerodynamic diameter rather than actual physical diameter. Aerodynamic diameter includes the inertial characteristics of airborne particles in size distribution results. This method also accounts for the effects on particle transport caused by the shape of the individual particles that make up the aerosol.

Fog oil aerosols were sampled periodically during the tests using two Andersen ambient-style cascade impactors operated at approximately 28 lpm. These devices provided separation of the aerosols by particle size into eight different aerodynamic size classifications ranging from approximately 0.5 to 10  $\mu\text{m}$ . Samples were drawn from the wind tunnel 6 m downwind of the test section, an area of low wind speed. This allowed accurate sampling of

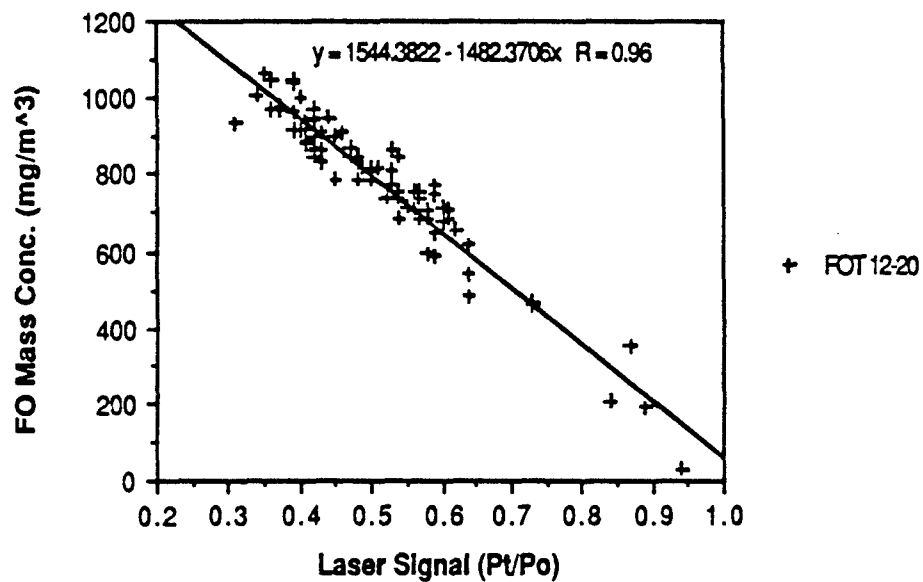
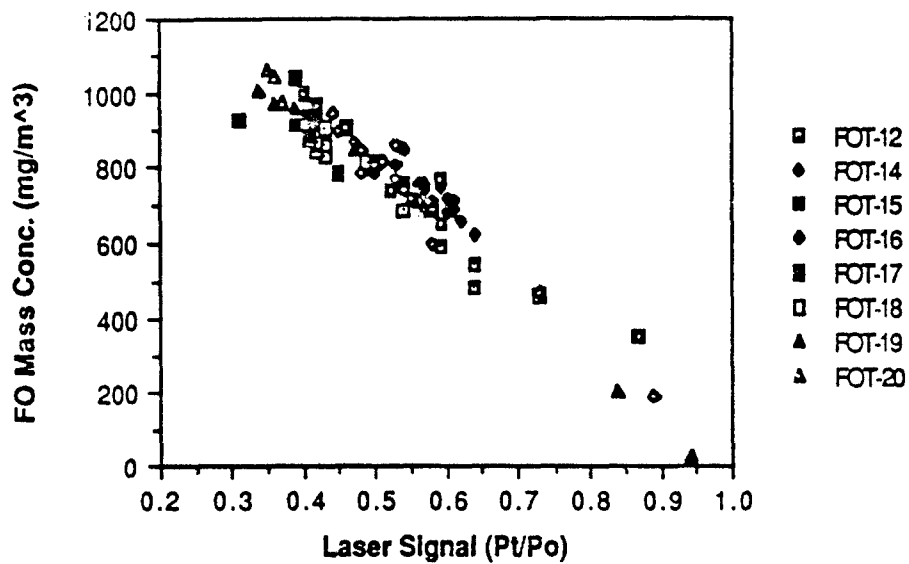


FIGURE 2.4. RESULTS OF LASER TRANSMISSOMETRY CALIBRATIONS DURING FOT-12 THROUGH FOT-20

**TABLE 2.2. LINEAR CALIBRATION PARAMETERS FOR LASER TRANSMISSOMETER MEASUREMENTS OF FOG OIL AEROSOL MASS CONCENTRATION.**  
 FORM OF EQUATION:  $C_m [mg/m^3] = \text{Slope} \times (P_t/P_o) + \text{Intercept}$ .  
 COEFFICIENT OF DETERMINATION =  $R^2$ .

Test	Slope	Intercept	$R^2$
FOT-4	-2657	1193	0.94
FOT-5	-3625	1441	0.55(a)
FOT-12	-1560	1530	0.95
FOT-14	-1780	1770	0.87
FOT-15	-1680	1660	0.90
FOT-16	-1650	1640	0.93
FOT-17-20	-1680	1620	0.98
FOT-22	-1835(b)	1683(b)	-
FOT-23	-1822	1721	
FOT-24	-2163	1903	
FOT-25	-1943	1789	
FOT-26	-1905	1751	
FOT-27	-1959	1779	
FOT-28	-1843	1670	
FOT-29	-1901	1706	
FOT-30	-1621	1490	

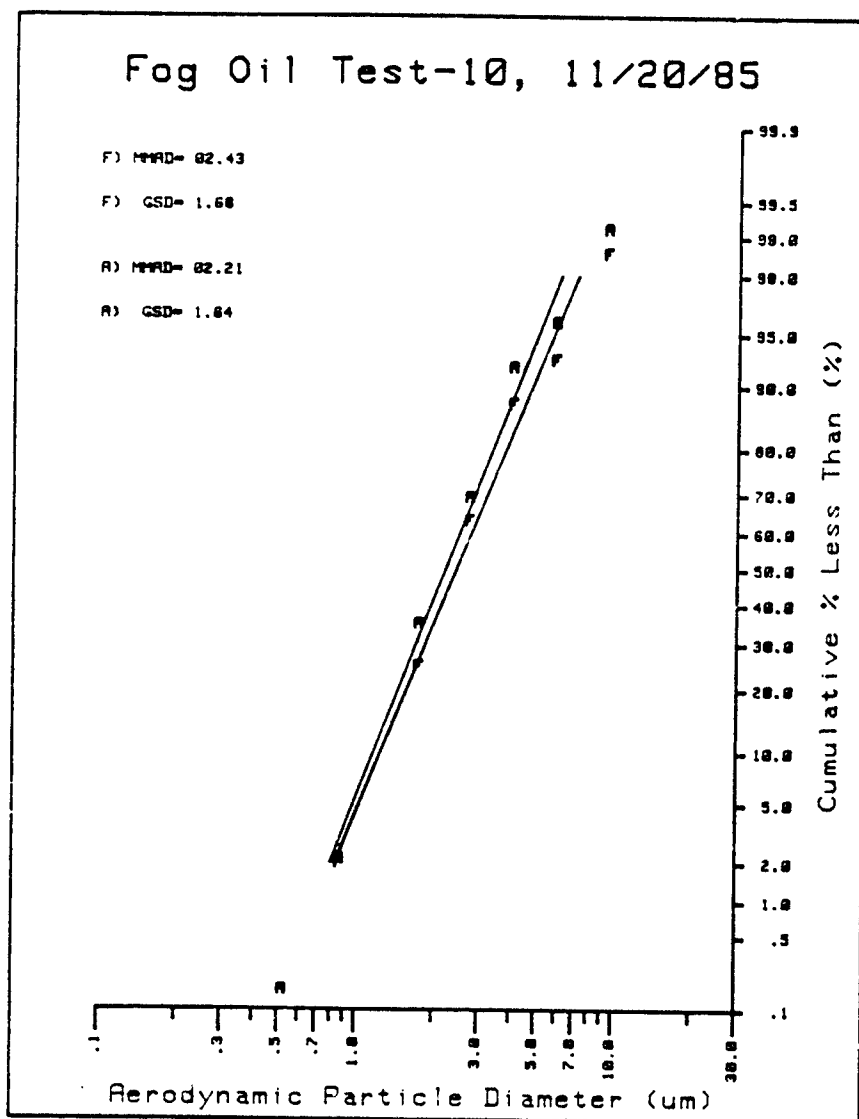
(a) Low  $R^2$  value attributed to limited FO concentration range (650-900  $mg/m^3$ ).

(b) No data for FOT-22, parameters equal to averages of tests 23 - 30.

the larger particles in the aerosols. Each impactor stage was covered with a pre-weighed, flat glass fiber substrate which was used to collect the particulate mass. Substrates were weighed after each sample, and the particulate mass, and with the sampling flow rate were analyzed for particle size statistics. One measurement was completed using flat thin-plate aluminum foil substrate to demonstrate potential errors associated with the rougher surface of the glass fiber filter substrate. The results of this comparison validated the use of glass fiber substrate, and indicated no large deviation in measurements of either mass median aerodynamic diameter (MMAD) or geometric standard deviation (GSD), and are shown in Figure 2.5.

## 2.5 FOG OIL CHEMICAL ANALYSIS

Several procedures were initially evaluated for quantification of fog oil hydrocarbons. GC-FID methods, while enabling resolution in individual components, was inappropriate for



**FIGURE 2.5. COMPARISON OF RESULTS OF CASCADE IMPACTOR OPERATION USING FLAT ALUMINUM AND GLASS FIBER COLLECTION SUBSTRATE**

mass quantitation in environmental matrices. IR absorbance was subject to substantial interference with extractable plant hydrocarbons and was also found to be unsuitable. To address the need for a rapid and sensitive method for total fog oil hydrocarbon analysis, a high performance liquid chromatography (HPLC) method was developed. This method was employed for all samples including soils, plant foliage, filter samples, and air samples. Where appropriate, fog oil and collected fog oil deposits were analyzed by gas chromatography to compare the stock liquid with that collected from the deposited aerosol.

The extraction and HPLC procedures developed were amenable to all matrices. Briefly, samples being analyzed (0.5 to 1 gm) were extracted in 5 mL isooctane, and total hydrocarbon determined by separation isocratically on a  $\mu$ Porasil column. Each run was 15 min long, with hydrocarbon retention time being 5.5 min. The mobile phase contained 5% ethyl acetate in isooctane, flow rate 1.5 ml/min, with detection at 230 nm. This procedure was rapid, requiring only 5-min extraction followed by direct analysis, and eliminates the majority of interference from natural plant hydrocarbons. Detection limits with this procedure are more than adequate (5  $\mu$ g FO/g sample), without concentration or manipulation.

## 2.6 PLANT AND SOIL SELECTION AND CULTIVATION

### 2.6.1 Plant Selection and Cultivation

The native species, including sagebrush, ponderosa pine, and short needle pine, are found associated with different training environments throughout the United States or used in revegetation, while bush bean (used as a sensitive indicator species for soft crops), the pines, and grass are important agronomic species found adjacent to many training installations. Plant sources and characteristics are as follows:

- Big Sagebrush (Artemisia tridentata vaseyana). A medium-sized, perennial shrub found over vast expanses of the arid and semi-arid western states. It grows in relatively harsh environments on alkaline soils and at elevations from sea level to 7000 ft. Source: Native Plants Inc., Sandy, Utah. Age: 2-year-old seedlings.
- Ponderosa Pine (Pinus ponderosa). A large coniferous tree, common to western North America. It grows at a wide range of elevations and is relatively tolerant to drought. It requires moderate soil fertility. Source: MacHugh Nursery, Eltopia, Washington. Age: 2-year-old seedlings.
- Short Needle Pine (Pinus echinata). A coniferous tree indigenous to the southeastern United States. This variety is used extensively in reforestation. Source: J.P. Rhody Nursery, Gilbertsville, Kentucky. Age: 2-year-old seedlings.
- Tall Fescue (Festuca elator). An ubiquitous perennial, cool season bunchgrass that grows well on dry or wet, alkaline or acid soils. Source: Native Plants, Sandy, Utah. Grown from seed.
- Bush bean (Phaseolus vulgaris, tendergreen). An agronomic species that is relatively sensitive to chemical insults, based on our experience. Grown from seed.



These five species provided a range of canopy types and cuticular structures and thicknesses for evaluating phytotoxic responses to obscurant smokes. Their foliar types and canopy structures are sufficiently different to permit evaluation of deposition velocities under a range of environmental conditions. Ponderosa pine, short needle pine, and sagebrush were maintained in the greenhouse prior to use. These species were allowed to go dormant in the fall of the year; in December, the greenhouse temperature was increased and photoperiod was artificially adjusted to break dormancy. Prior to their experimental use in the spring, groups of these plants were transferred to growth chambers and allowed to equilibrate for 30 days, where they were maintained at day/night temperatures of 32°/21°C, a 16-hr photoperiod (approximately 500  $\mu\text{E m}^{-2} \text{ sec}^{-1}$ , PAR, at leaf surface), and 50% relative humidity. Bush bean was planted and grown in growth chambers under the same conditions. Tall fescue was grown from seed and maintained at day/night temperatures of 27°/15°C, a 10-hr photoperiod (approximately 500  $\mu\text{E m}^{-2} \text{ sec}^{-1}$ , PAR, at leaf surface), and 50% relative humidity.

Both pine species were grown on a commercially available loam soil, while the sagebrush, tall fescue, and bush bean were grown on Burbank sandy loam. The latter plants were used to evaluate direct foliar contact toxicity, and at no time was the soil of these test systems exposed to fog oil.

#### 2.6.2 Soil Selection and Characteristics

Two soils were used to evaluate indirect soil/plant effects. For this evaluation, soils were contaminated with fog oil smokes prior to the seeding and growth of the grass species. The two soils used were Burbank (found at Hanford, Washington), an alkaline sandy loam that readily supports the growth of the grass species; and Maxey Flats (found at Morehead, Kentucky), a silty-clay that is noncultivated, has low nutrient status, and will support marginal growth of the grass species. All soils were maintained at 50 to 66% of field capacity prior to and following experimental use. Their physical and chemical characteristics are provided in Table 2.3. In addition, a Palouse silt loam typical of eastern Washington agricultural areas, was used for the microbial tests.

**TABLE 2.3. SELECTED PROPERTIES OF TEST SOILS**

Soil Property	Burbank Sandy Loam	Maxey Flats Silty-Clay
pH	7.43	8.43
Organic carbon (%)	0.52	0.74
Sulfur (%)	0.060	0.025
Nitrogen (%)	0.070	0.095
Total phosphorus ( $\mu\text{g/g}$ )	2400.	716.
$\text{PO}_4^{3-}\text{-P}$ ( $\mu\text{g/g}$ )	4.8	6.7
Fine and coarse clay (%)	4.0	33.4
$\text{CO}_3^{=}\text{ + HCO}_3^{-}$ (%)	<0.5	4.65
$\text{NH}_4^{+}(\text{N})$ ( $\mu\text{g/g}$ )	6.1	99.

## **2.7 PLANT/SOIL MEASUREMENTS**

### **2.7.1 Foliar Contact Toxicity Responses**

In evaluating direct foliar contact toxicity, plant canopies were exposed to smokes under a range of concentration, time, and atmospheric conditions. In all cases, soils were isolated from canopies by bagging the soil containers at the lower plant stem to preclude any indirect effects arising from soil contamination. All foliar exposures were conducted in the illuminated portion of the wind tunnel test section.

Toxicity responses arising from direct contact of smokes with foliar surfaces, namely those that are readily visualized or phenotypic, were evaluated using a modified Daubenmire Rating Scale (DMRS) (Table 2.4). This nonparametric approach provides for a rapid comparison of gross toxicity and its relative intensity with time of post-exposure. In addition, grasses that are harvested 3 to 4 wk after exposure (direct canopy effects) were permitted to regrow through one or more subsequent harvests, and dry matter production was monitored. Regrowth and monitoring allows for evaluation of any residual plant effects resulting from foliar absorption and root accumulation of smoke components.

### **2.7.2 Indirect Plant Effects**

Indirect plant effects were evaluated by exposing Burbank and Maxey Flats soils to smoke aerosols. These soils (444 and 526 g dry weight of Maxey Flats and Burbank, respectively) were brought to moisture level, placed into 4.5-in.-diameter by 4-in.-high pcts, the

**TABLE 2.4. CODING FOR MODIFIED DAUBENMIRE RATING SCALE AND ASSOCIATED PHYTOTOXICITY SYMPTOMS**

Symptom/intensity	Description
<u>Modified Daubenmire Rating Scale</u>	
0	no obvious effects over controls
1	between 0-5% of foliage affected
2	between 5%-25% of foliage affected
3	between 25%-50% of foliage affected
4	between 50%-75% of foliage affected
5	between 75%-95% of foliage affected
6	between 95%-100% of foliage affected
<u>Phenotypic Responses</u>	
OGA	old growth affected
NGA	new growth affected
O&NGA	old and new growth affected
TB	tip or leaf edge burn
LBD	leaf burn and leaf drop
NS	necrotic spotting
LD	leaf abscission or needle drop
CH	chlorosis
BD	blade dieback
LC	leaf curl
W	wilting
GD	growing tip dieback
D	plant dead
FSA	floral or seed/fruit abortion
(+ value)	indicates the length in cm that needles or leaves exhibit dieback or burn

surfaces leveled, and pots were exposed to smokes. Four days after being exposed, the soils were seeded with 15 tall fescue seeds. This approach resulted in contamination of only the soil surface; post-planting irrigation should result in some redistribution of smoke components down the soil profile. Indirect plant effects resulting from smoke contaminants deposited to soils were determined by evaluating the percentages of germination and dry matter production using tall fescue as a test species. Dry matter production for plants grown on contaminated soils was followed through two or more harvests.

### 2.7.3 Quantitation of Exposure/Dose

The evaluation of plant toxicity responses to airborne contaminants requires a basis for intercomparison of treatments and variables. In all of the toxicity studies, the point of reference is the mass loading value or exposure dose, as opposed to air concentration or exposure duration, to provide a specific dose value for each plant. The mass loading rate is determined by chemical measurement of the amount of smoke deposited to a unit area or weight of foliage,

and is an absolute index of dose. In the case of fog oil smokes, total foliar fog oil hydrocarbons was determined by extraction of foliar samples (0.5 to 1 g) with 5 ml isooctane. Mass loading to soils was estimated based on loading to filter coupons, dry Petri dishes, and wet Petri dishes followed by extraction as noted earlier. Quantitation of interception efficiency for the type of receptor surface is based on computed deposition velocities (namely the type of canopy structure). The velocities are calculated from the air concentration, exposure duration, and the quantity of smoke (hydrocarbons) deposited per unit surface area.

The rates at which aerosols are deposited to the plant and soil surfaces in the wind tunnel, or the deposition velocities, were determined as functions of the fog oil mass concentration of the aerosols, mass deposited, and exposure duration. Deposition velocity results were compared for exposure variables including duration, relative humidity and wind speed.

#### 2.7.4 Post-Exposure Simulated Rainfall

The intensity of phytotoxic responses to foliar contaminants can be modified by the presence or absence of surface moisture. Immediately following exposure, subsets of exposed plants were subjected to a "simulated rainfall" (Figure 2.6) equivalent to 1.0 cm, as described in Cataldo et al. (1981). Use of post-exposure simulated rainfall permitted evaluation of either the ameliorating effects of foliar leaching (surface wash-off), or any intensification of effects resulting from the presence of surface moisture and increased foliar uptake. This experimental procedure was performed for all test series, except the "rain-out" portion of the Relative Humidity Test Series, where simulated rainfall was applied during aerosol exposure.

#### 2.8 SOIL MICROBIOLOGICAL MEASUREMENTS

Large petri-dishes (150 x 15 mm) containing 50 g of air-dried Burbank (sandy, skeletal, mixed, xeric, Torriorthent) sandy loam or Palouse (fine-silty, mixed, mesic, Pachic Ultic Haploxeroll) silt loam soil were moistened with 10 ml of distilled water. For the relative humidity test series, the soils were exposed to fog oil obscurant smoke at 20%, 64%, and 91% relative humidity (FOT-12, FOT-14 and FOT-15, respectively) for 4 hr at a wind speed of 2 mph in the PNL Toxic Aerosol Test Facility according to the described test protocol. Concentrations of fog oil at these exposures ranged from 730 to 830 mg/m<sup>3</sup>. For the 10-mph wind speed test (FOT-18), soil was exposed to fog oil for less than 1 hr at a mass concentration of 940 mg/m<sup>3</sup>. For the cumulative dose test, soil was exposed nine times (one time each at 3 and 4 hr, and 7 times at 2 hr) for a total exposure time of 21 hr at a wind speed of 2 mph over a period of 18 days (FOT-22b through FOT-30b). Mass concentrations of fog oil smoke ranged from 350 to



FIGURE 2.6. POST-EXPOSURE SIMULATED RAINFALL SYSTEM

670 mg/m<sup>3</sup> during these exposures. Soil moisture lost during each exposure was measured by weight loss and replaced by adding deionized water immediately after each exposure. Average moisture loss was about 15% after each exposure. Table 2.5 lists the exposure conditions and aerosol characteristics for these tests.

Soil respiration of the Palouse soil was measured with an electrolytic respirometer incubation system described by Knapp et al (1983). After the exposure, the smoked and control Palouse soils were transferred to pint-size Mason jars. Control and exposed soil received 2 ml of distilled water while another control soil received 2 ml of 75 mg/ml glucose solution. Oxygen consumption by the soil was measured manometrically with the electrolytic respirometers at a controlled temperature of 20°C. Respiration was measured periodically for up to 2 wk. Measurements were obtained for two replicate samples of each treatment and control soil.

Soil dehydrogenase activity was assayed by a modification of the method of Tabatabai (1982). Aliquots of soil (1.5 g wet weight) were first mixed with 0.015 g of CaCO<sub>3</sub>, 0.3 ml of 1% glucose or casamino acids and 0.25 ml of the substrate, 2,3,5-triphenyltetrazolium chloride (3% w/v). After incubation at 22°C for 24 hr, 10 ml of methanol was added to the soil to extract the product, 2,3,5-triphenylformazan (TPF). The solution was mixed thoroughly, centrifuged, and the absorbance of the supernatant determined at 485 nm. Soil dehydrogenase activity, expressed as µg of TPF produced per g of dry soil per 24 hr, was determined by comparing absorbance values to a standard curve prepared with reagent grade TPF and methanol. Dehydrogenase activity was measured in triplicate, and mean values were compared with that of the control (unexposed) soil and expressed as a percent of the control.

Soil nitrifying bacteria were enumerated by the microtechnique for most-probable-number analysis (Rowe et al. 1977) using media described by Alexander and Clark (1965). Ammonium-calcium carbonate medium for *Nitrosomonas* consisted of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.5 g; K<sub>2</sub>HPO<sub>4</sub>, 1.0 g; FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.03 g; NaCl, 0.3 g; MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.3 g; and CaCO<sub>3</sub>, 7.5 g in 1000 ml distilled water. Nitrite-calcium carbonate medium for *Nitrobacter* consisted of KNO<sub>2</sub>, 0.006 g; K<sub>2</sub>HPO<sub>4</sub>, 1.0 g; FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.03 g; NaCl, 0.3 g; MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.1 g; CaCl<sub>2</sub>, 0.3 g; and CaCO<sub>3</sub>, 1.0 g in 1000 ml distilled water. The media were autoclaved at 15 lb pressure for 30 min. Aliquots (0.2 ml) were transferred to 25 wells of a sterile microplate. A 10-fold serial dilution of soil was prepared with sterile 0.35% saline solution. Five wells were inoculated with 0.1 ml of 10<sup>-2</sup> through 10<sup>-6</sup> dilutions with five replicates at each dilution. After incubation for 6 wk at room temperature in the dark, wells containing ammonium-calcium carbonate medium for *Nitrosomonas* were tested for the presence of nitrite and/or nitrate using the modified

**TABLE 2.5. CHARACTERISTICS FOR FOG OIL SMOKE TESTS EMPLOYED IN THE STUDY OF MICROBIOLOGICAL EFFECTS**

Test No.	Date	Temperature (°C)	Wind Speed (mph)	Exposure Time (hr)	Relative Humidity (%)	Aerosol Mass Concentration (mg/m <sup>3</sup> )
FOT-12	11/22/85	22.4	2	4	20	730
FOT-14	11/26/85	21.9	2	4	64	740
FOT-15	12/02/85	22.0	2	4	91	830
FOT-18	12/17/85	21.4	10	0.75	72	940
FOT-22b - 30b (CDT)	2/00/86 through 2/24/86	22.1-25.0	2	2 to 4 total of 21 hr	56 to 61	350 to 670 each run

Griess-Illosvay and nitrate spot test reagents described by Schmidt and Belser (1982). Positive tests for nitrite/nitrate in these tubes indicate the presence of *Nitrosomonas*. Wells containing nitrite-calcium carbonate medium were tested for nitrite. A negative test for nitrite indicated the presence of *Nitrobacter*. Populations of both groups of nitrifying bacteria were calculated using a most-probable-number (MPN) table (Alexander 1982) and presented as the log<sub>10</sub> of MPN per g of dry soil.

## 2.9 SOIL INVERTEBRATE MEASUREMENTS

An earthworm (*Eisenia fetida*) bioassay system was used to elucidate the toxicity of the fog oil. An artificial soil containing 350 g sand, 100 g Kaolin and 50 g dried peat moss (adjusted to pH 6.5 with CaCO<sub>3</sub>), was used for the earthworm exposures. Worms were fed twice weekly with fermented alfalfa, and soil moisture adjusted to 35% of dry weight. These soil tests used 80 g of the artificial soil (placed in 100 x 25 mm Petri plates), containing 6 worms. Two or three replicate plates were used for each test series as noted in the text. The tests were terminated after 14 days, and effects observed over this period. Effects scored included both earthworm mortality and cocoon hatch. Mass loading or dose was determined on similar soil plates without worms.

*In vitro* studies were also conducted. In this study the artificial soil was amended with sufficient fog oil to simulate doses of 0 to 7275 µg FO/cm<sup>2</sup>. Five worms were added to each of three replicate treatments, and mortality was determined after 7 days.

### 3.0 RESULTS AND DISCUSSION

The evaluation of the environmental fate and effects of fog oil obscurant was approached in a systematic manner. This permitted investigation under a range of simulated environmental conditions, using a wind tunnel to provide a means for dynamic exposure of test systems. While the primary emphasis was on terrestrial effects, an understanding of the chemistry of these smokes is essential, particularly from the standpoint of smoke generation, kinetics of transformation while in residence within the wind tunnel, and following deposition to soils and vegetative surfaces. To adequately address these needs, experiments were performed to determine 1) the physical and chemical characteristics of aerosols, 2) the influence of environmental/ experimental conditions including relative humidity, wind speed and exposure duration on mass loading to receptor surfaces (soils and plant foliage), and 3) the influence of these variables on key biotic processes.

Briefly, the approach employed for fog oil smoke was, first to establish a burn or combustion configuration that approximated the normal limits for field generation of the smoke. For example, with fog oil, combustion temperature and oxygen concentration will influence the airborne hydrocarbon pattern resulting from thermal and "cracking" processes, respectively. Second, simultaneously with the later stages of these set-up efforts, detailed physical and chemical characterization of the smokes was undertaken. This included characterization of smoke aerosols in time (time of exposure, 0 to 8 hr), their comparative fate once deposited to foliage, and their short-term fate following deposition to soil surfaces. This information, while needed to adequately understand and define any observed adverse environmental effects, was essential for establishing base line conditions for intercomparisons with past studies and/or future efforts.

This approach permitted a greatly reduced analytical effort in subsequent experiments, with detailed chemical characterization being performed on an "as needed basis." Following the generation and delivery set-up studies, and detailed chemical characterization efforts, a series of four discrete experimental tests were performed to address a range of either dosing conditions or environmental variables on terrestrial smoke effects. The actual experimental tests included:

- Range Finding Test. This test series established a suitable air concentration and mass loading rate for vegetative surfaces that elicited some detectable effect. Experimentally this involved the exposure of plants at a single smoke concentration for 2, 4, 6, and 8 hr. Depending on the point at which effects are noted, the mass loading value, exposure time, and air concentrations were used to calculate the appropriate critical air concentration for subsequent routine 4-hr exposures. Data output from this experiment included, in addition to



critical air concentrations, preliminary toxicity response data, mass loading levels with time, and deposition velocities for the smokes. No soil effects efforts were undertaken, nor were rainout or simulated post-exposure rainfalls performed for this test.

- Cumulative Dose Test. The purpose of this test was to determine whether a series of cumulative low doses/mass loadings are as toxic as a single large dose. This involved repeated exposure of plants and soils to individual smokes, at a low and high fog oil concentration, three times per week for a 3-wk period, or nine consecutive exposures. No rainout or simulated rainfall were performed; however, all other data were collected, including grass regrowth, the full set of indirect effects resulting from soil contamination and microbiological tests. This test series evaluated the cumulative effects of repeated exposure, and provided the greatest extent of foliar and soil loading.

- Relative Humidity Test. This test series was designed to evaluate the effect of RH on deposition to foliage and smoke toxicity. This environmental parameter was important because the effect of moisture on both particle growth and biological availability, particularly with hygroscopic smokes. All quantitative and plant toxicity parameters were determined, including soil, microbial, and earthworm impacts.

- Wind Speed Test. The final test of the series involved evaluation of the effect of wind speed on the phytotoxicity of smokes, and calculation of deposition velocities for these simulated atmospheric conditions. The importance of wind speed was first noted in the phosphorus studies (Van Voris et al. 1987), and is an excellent example of an accelerated mass loading resulting from a shift from diffusional and gravitational based deposition to impaction, which results in much higher mass loadings and effects. The only parameters followed were toxicity, the ameliorating effect of post-exposure simulated rainfall, grass regrowth, and the deposition parameters.

### 3.1 FOG OIL CHEMICAL ANALYSIS

Analyses of environmental samples for total oil were historically developed as a result of oil spills in the ocean. These methods generally involve extraction of the sample with a solvent and determining the spectrophotometric absorbance of the extract. One of the most commonly used methods is the infrared absorbance (IR) technique, in which the sample is extracted with carbon tetrachloride and the absorbance at 2729 reciprocal cm determined. Preliminary experiments with plant leaves indicated that there was sufficient carbon tetrachloride extractable endogenous organic material in plant leaves to constitute a possibly unacceptable

blank. Figure 3.1 shows the IR absorbance spectrum of carbon tetrachloride extracts of leaves from four plant species, compared to a fog oil solution. As a consequence of this observation, further experiments were designed to select the most appropriate analytical method for oil on leaf tissue.

In addition to the IR method, three other methods were investigated: ultraviolet (UV) absorbance, liquid chromatography (LC), and gas chromatography (GC). The studies were performed on leaves from four plant species (a grass, soybean, sagebrush, and pine) which had been exposed for 4 hr to a  $10\text{-g/m}^3$  concentration of fog oil aerosol in a static chamber. Individual leaves (five leaves in the case of sagebrush) were taken for analysis both before and after exposure for each of the methods to be studied. Both exposed and unexposed leaves were analyzed in duplicate. Each leaf sample was extracted in a Corex tube for 10 minutes with 5 ml solvent: for IR, carbon tetrachloride was used; for the rest, isooctane. Analyses of extracts were conducted as follows:

- IR Method - the infrared spectrum was obtained from 3400 to 2400 reciprocal cm. The difference between percent transmitted at baseline and maximum absorbance at 2927 reciprocal cm was converted to absorbance, and the oil concentration determined by reference to a calibration curve constructed from known concentrations of fog oil.

- UV Method - the ultraviolet absorbance at 230 nm was determined on isooctane extracts. Oil concentration was determined from a calibration curve constructed using known concentrations of oil.

- LC Method - a 5- $\mu\text{l}$  sample of isooctane extract was injected onto a silica liquid chromatography column (Waters  $\mu\text{Porasil}$ , 25 cm). The sample was eluted with 1.5 ml/min isooctane/ethyl acetate. Detection was by UV detector set at 230 nm. The peak area ( $RT = 5.5$  min) was compared with that from a standard to determine concentration of oil and interfering material eluted just prior to and after the fog oil peak (Figure 3.2).

- GC Method - a 1- $\mu\text{l}$  sample of isooctane solution of fog oil was injected onto a 15-m capillary GC column (SE-54) using a 10:1 split ratio. Initial oven temperature was  $100^\circ\text{C}$ . Immediately upon injection, temperature was raised to  $280^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . The oil eluted from the column as a single unresolved envelope with small sharp peaks superimposed. This resulted in difficulties in integrating the area under the envelope. A calibration curve of known quantities of oil was nonlinear, and there was some evidence that injection port contamination occurred. This method was not pursued further in view of better results with the LC method.

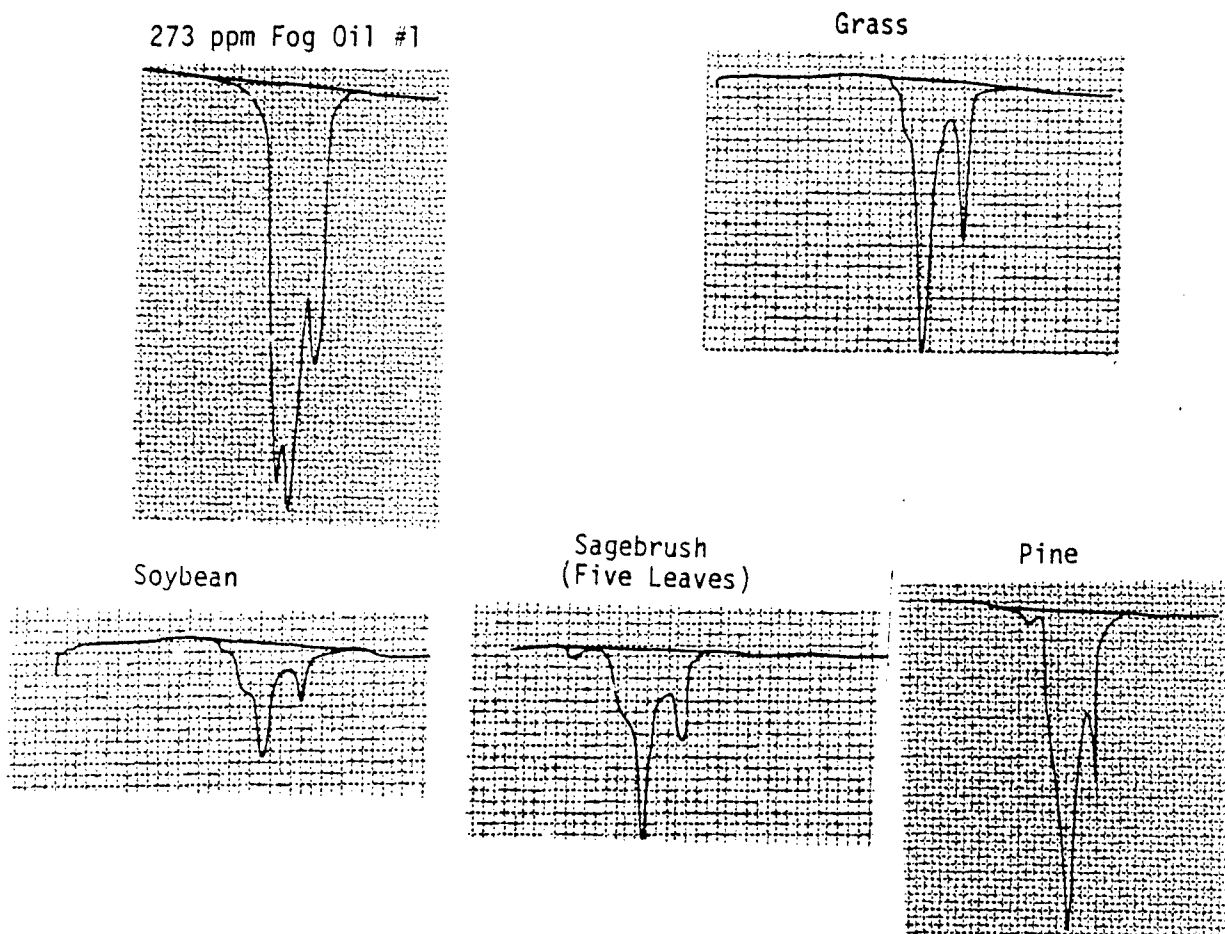


FIGURE 3.1. INFRARED ABSORBANCE OF FOG OIL CONTAMINATED AND UNEXPOSED LEAVES

Following extraction for oil, leaf samples were removed from solvent, pressed flat, and the surface area determined. Oil quantities were reported in terms of mg oil per square cm. Quantities of oil reported were corrected for values determined from unoiled leaves. Table 3.1 shows values in terms of equivalent milligrams of oil obtained from unoiled leaves. The very high values obtained for the IR and UV methods, particularly for sage and pine, do not recommend these as methods of choice, in view of the quantities of oil found on the oiled leaves (Table 3.1). Blanks for pine, for example, have between 11 and 35% of the reported oil burden for these methods. On the other hand, the LC method does not yield a high blank, and gives results that are in general comparable to the absorbance methods (Table 3.1). The LC

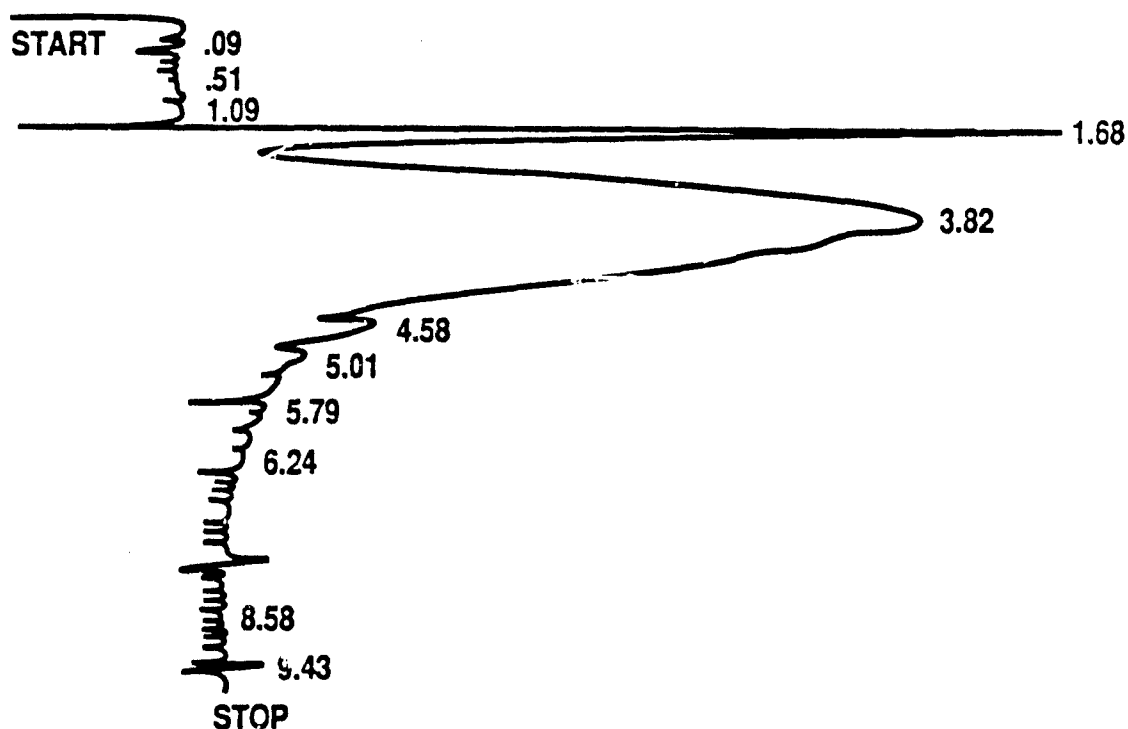


FIGURE 3.2. LIQUID CHROMATOGRAM OF FOG OIL ANALYSIS (90 µg/ml)

TABLE 3.1. DETECTION METHODS AND SIGNAL RESPONSES FOR UNOILED AND OILED LEAVES

Leaf Type	IR	UV	LC	GC
	( mg FO/cm <sup>2</sup> Foliage)			
<u>Unoiled</u>				
Soybean	0.005	0.097	ND(a)	0.026
Sagebrush	0.414	0.277	ND	ND
Grass	0.122	0.086	ND	ND
Pine	0.581	0.565	0.043	0.020
<u>Oiled</u> (duplicates, corrected for blanks)				
Soybean	2.8, 5.1	6.6, 3.7	3.9, 5.3	NI(b)
Sagebrush	6.3, 5.4	4.1, 5.7	3.8, 5.7	NI
Grass	6.8, 10.4	3.3, 2.4	1.3, 3.1	NI

(a) ND, not detected

(b) NI, not interpretable

values for grass were lower than those obtained with UV or IR. Since close agreement was obtained with the other three species, it is likely that the results with grass were because of sample variability, which was in general higher than observed with phosphorus deposition. The relatively high variation from sample to sample may be a consequence of the static exposure regime.

As a result of these preliminary investigations, HPLC was assessed the method of choice for total fog oil due to the lack of interference by plant products, sensitivity and reproducibility. The method as used in this work can easily detect 0.1 mg FO/cm<sup>2</sup> of leaf surface and can be made more sensitive if required. Blanks are acceptably low.

Comparison of the mass of fog oil determined gravimetrically with that measured chemically from selected aerosol samples indicated a variability, or potential source of error (Table 3.2). These measurements were made during tests FOT-12, 14, 15, 16, 17, 18, 19, and 20. While the ratio of fog oil mass determined chemically to that determined gravimetrically varied from 0.97 to 1.42, the variability during any one test was generally small. Analysis for fog oil mass by chemical procedures resulted in an average of 1.16 times more fog oil than was determined by the gravimetric analysis.

### 3.2 SMOKE (AEROSOL) CHARACTERIZATION

Fog oil aerosols were characterized during exposure tests primarily to provide information on their concentration and particle size distribution. These data were then compared to environmental conditions and ecological effects, and included mass loading rates to plants, soils, and other surfaces. Deposition velocities were calculated to relate environmental and aerosol characteristics to the rate of fog oil mass loading to the various surfaces.

#### 3.2.1 Physical Aerosol Characteristics

Aerosol mass concentration was maintained at approximately constant (or steady-state) conditions throughout each test by operating the generator at a single output after the initial high-generation period. Slight fluctuations, and trends toward greater or lesser aerosol concentrations during the tests indicated imperfect control and repeatability of aerosol generation. Figures 3.3 through 3.6 each include two records of actual fog oil aerosol mass concentration during a specific fog oil test series. Average aerosol mass concentration during each test was determined by applying the laser transmissometer calibration relationships to the data and is shown in Table 3.3.

**TABLE 3.2. COMPARISON OF FOG OIL MASS COLLECTED FROM AEROSOL SAMPLES CHARACTERIZED BY GRAVIMETRIC AND CHEMICAL PROCEDURES**

Test	No. of Samples	Fog Oil Mass Ratio: Mchem/Mgrav
FOT-12	3	1.06 ± 0.10
FOT-14	4	1.38 ± 0.05
FOT-15	4	1.13 ± 0.05
FOT-16	5	1.11 ± 0.04
FOT-17&18	3	1.10 ± 0.03
FOT-19&20	4	1.20 ± 0.02

Unlike aerosols of phosphorus compounds (Van Voris et al. 1987), the concentration of fog oil was not affected by the presence of water vapor as high humidity in the wind tunnel atmosphere. Aerosol mass concentrations were controlled in the range of anticipated field concentrations, 100 to 1000 mg/m<sup>3</sup>. Concentrations were between 690 and 780 mg/m<sup>3</sup> during the range-finding tests, between 730 and 870 mg/m<sup>3</sup> during the relative humidity tests, between 910 and 990 mg/m<sup>3</sup> during the wind speed tests, and between 68 and 135 mg/m<sup>3</sup> during the low-dose and 350 and 670 mg/m<sup>3</sup> during the high-dose cumulative dose tests.

Figure 3.7 shows relative exposure dose terms for the cumulative dose test series. These data indicate an average low dose exposure of 13,510 ± 2,280 (17%) mg-min/m<sup>3</sup> for the low-dose tests, and 72,260 ± 7,470 (10%) mg-min/m<sup>3</sup> for the high-dose series. In both cases, the uncertainty is equal to the standard deviation of the doses during all nine cumulative dose tests. It is important to use the dose term to compare the individual cumulative dose tests because of the differences in exposure duration required due to erratic generation operation. Exposure durations ranged from 110 to 240 min during the cumulative dose tests.

The particle size distributions of the fog oil obscurant aerosols maintained in the wind tunnel were characterized by measurements of MMAD and GSD. These two particle size parameters were adequate to completely describe the log-normally distributed fog oil aerosols. Particle size distribution measurements were obtained during all test series other than the 60-min duration wind speed tests, and results are summarized in Table 3.4. Actual distributions from each test series are shown in Figures 3.8 through 3.10.

As shown in Table 3.4, the particle size of fog oil aerosols was seen to increase strongly as a function of aerosol mass concentration, but did not increase strongly as a function of relative humidity. The influence of mass concentration on particle size was attributed to the coagulation of concentrated small particles and their subsequent growth into larger particles.

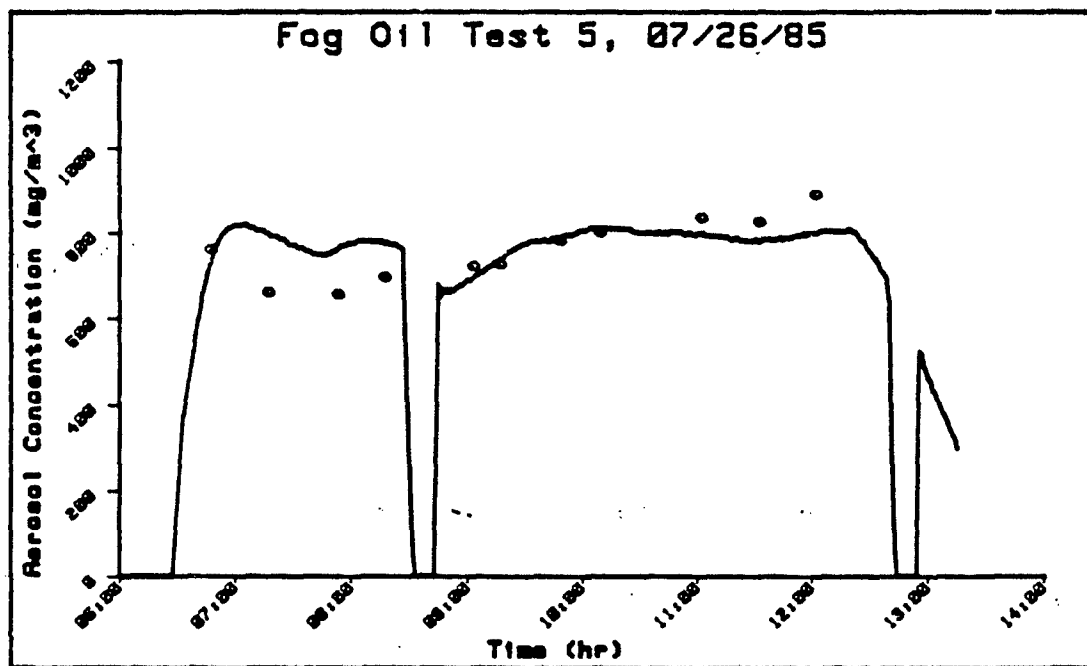
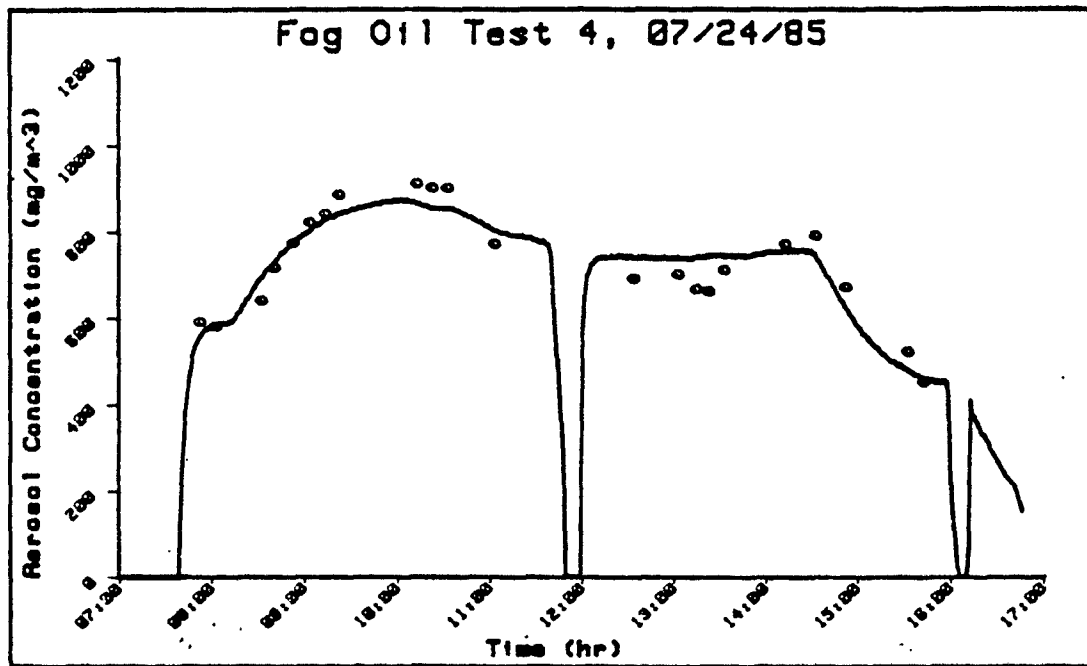


FIGURE 3.3. AEROSOL MASS CONCENTRATION VERSUS TIME FOR TWO FOG OIL RANGE-FINDING TESTS

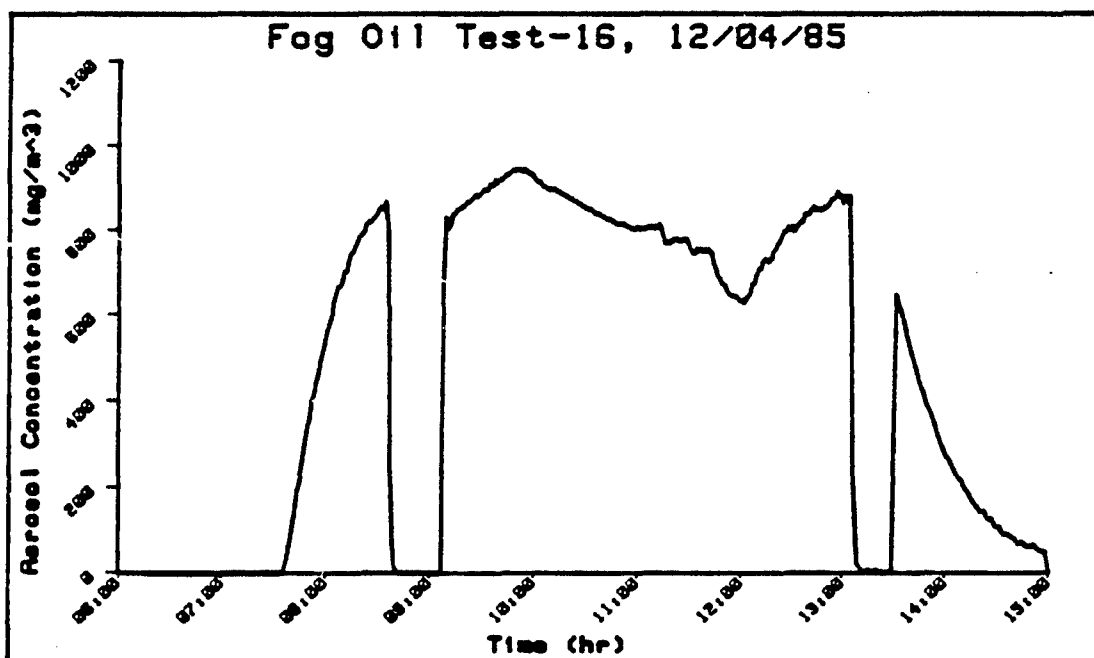
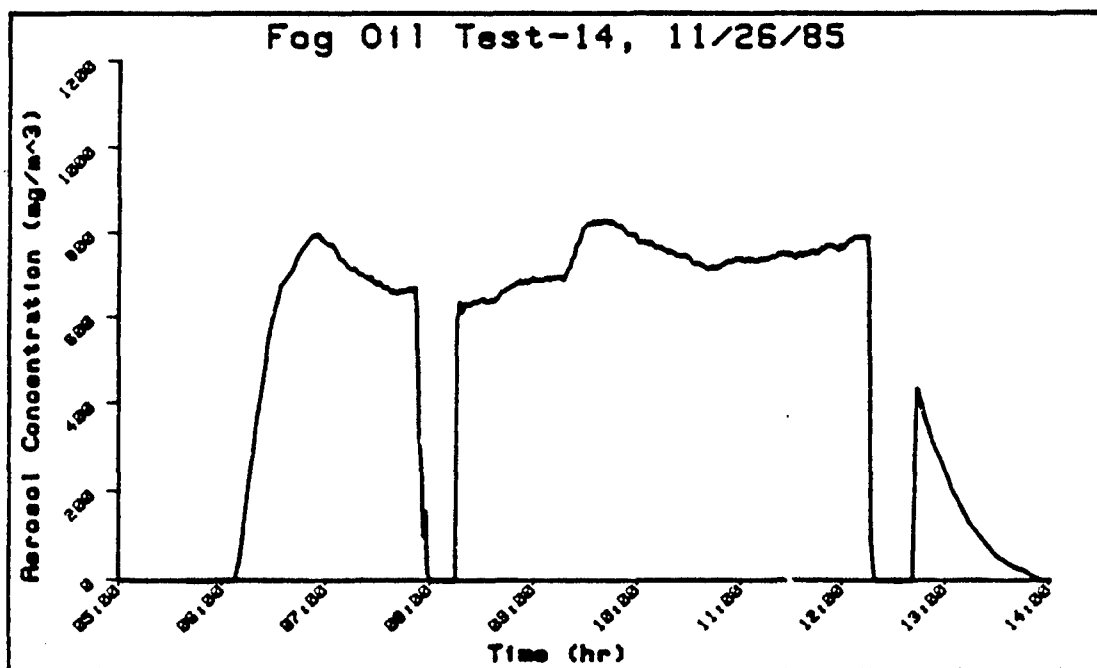


FIGURE 3.4. AEROSOL MASS CONCENTRATION VERSUS TIME FOR TWO FOG OIL RELATIVE HUMIDITY TESTS



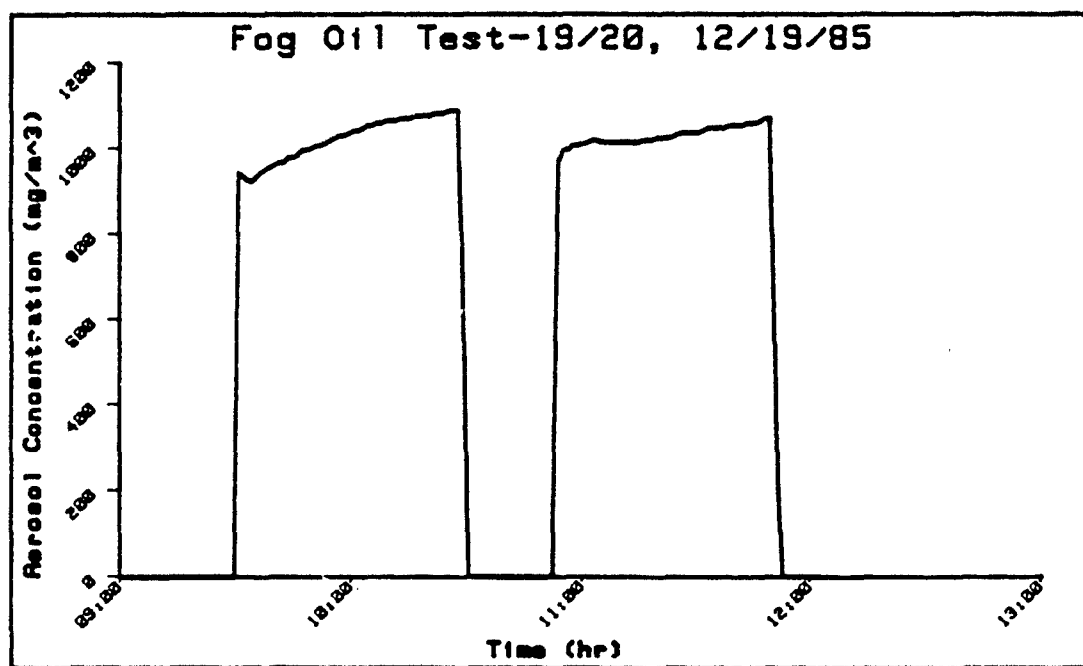
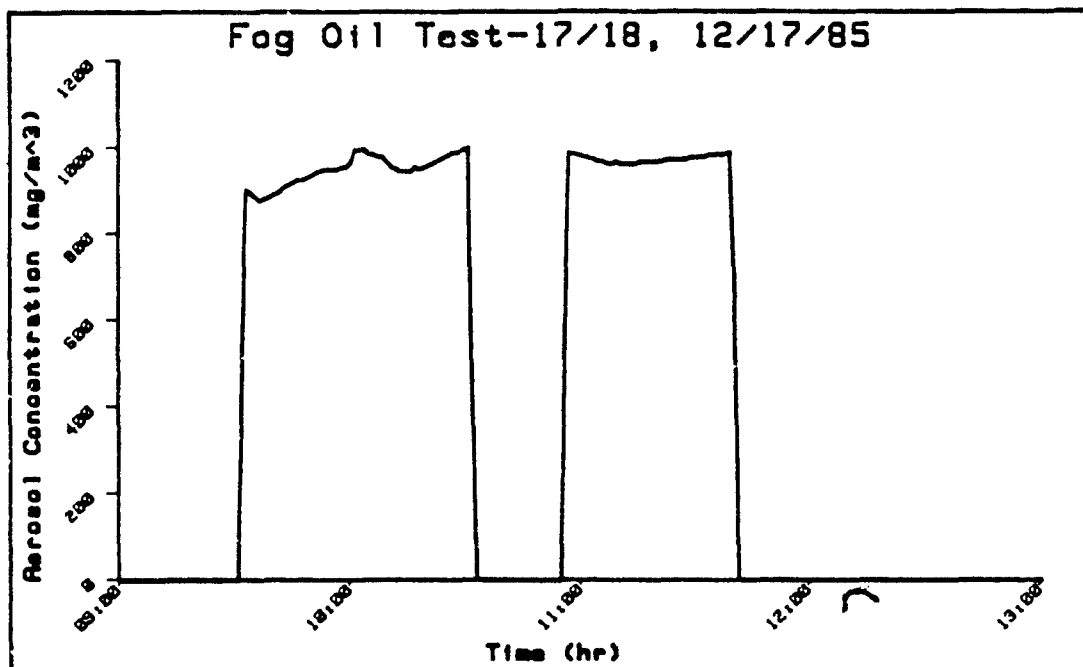


FIGURE 3.5. AEROSOL MASS CONCENTRATION VERSUS TIME FOR TWO FOG OIL WIND SPEED TESTS

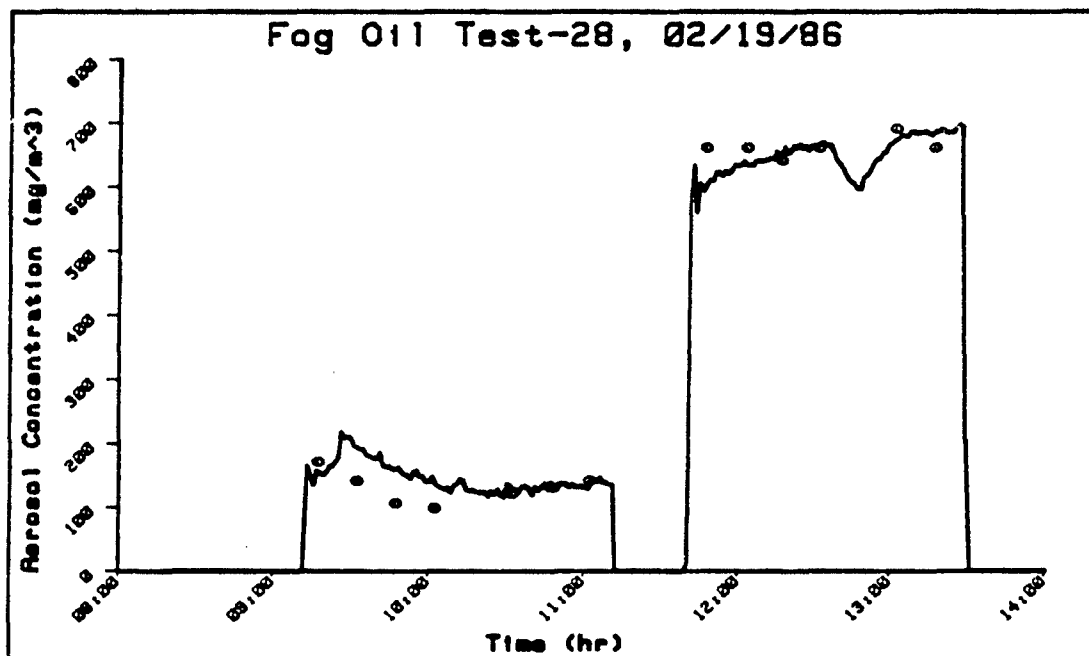
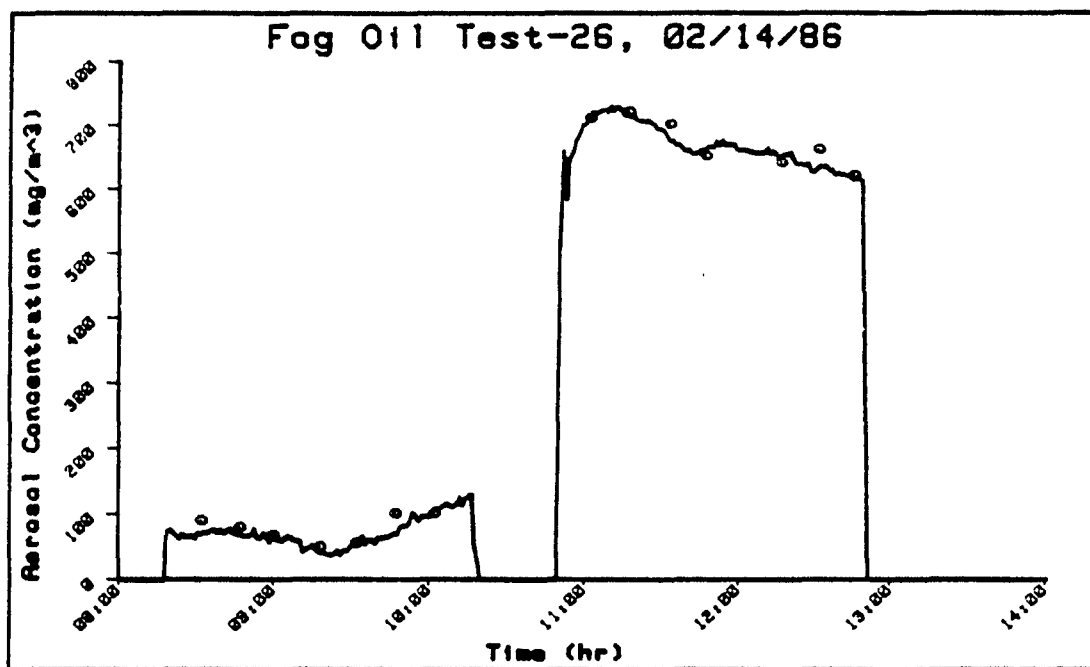


FIGURE 3.6. AEROSOL MASS CONCENTRATION VERSUS TIME FOR TWO FOG OIL CUMULATIVE DOSE TESTS

**TABLE 3.3. AVERAGE AEROSOL MASS CONCENTRATION DURING FOG OIL OBSCURANT TESTS**

Test	Temp. (~C)	Relative Humidity (%)	Wind Speed (m/s)	Aerosol Mass Concentration (mg/m <sup>3</sup> )
<b>Range-Finding</b>				
FOT-4-4	20.5	58	0.73	780
FOT-4-8	20.9	58	0.73	720
FOT-5-2	19.8	55	0.73	690
FOT-5-6	20.2	52	0.73	720
<b>Relative Humidity</b>				
FOT-12	22.4	20	0.90	730
FOT-14	21.9	64	0.90	740
FOT-15	22.0	91	0.90	830
FOT-16	22.3	74	0.90	810
FOT-16(dry)	22.8	61	0.90	870
FOT-16(rain)	21.7	86	0.90	760
<b>Wind Speed</b>				
FOT-17	22.4	66	0.91	910
FOT-18	21.4	72(a)	4.34	940
FOT-19	20.2	62	1.81	990
FOT-20	20.9	58	2.70	960
<b>Cumulative Dose</b>				
FOT-22a	23.0	59	0.91	68(b)
FOT-22b	22.3	61	0.90	350(b)
FOT-23a	22.8	59	0.90	110
FOT-23b	22.5	60	0.89	495
FOT-24a	22.6	62	0.88	113
FOT-24b	22.5	58	0.84	395
FOT-25a	22.5	64	0.91	73
FOT-25b	22.4	60	0.90	~560
FOT-26a	23.2	61	0.93	80
FOT-26b	23.1	56	0.86	670
FOT-27a	21.3	61	~0.9	108
FOT-27b	22.1	58	~0.9	645
FOT-28a	23.7	58	~0.9	130
FOT-28b	22.9	56	~0.9	645
FOT-29a	22.1	63	0.89	110
FOT-29b	22.3	60	0.91	585
FOT-30a	23.8	63	~0.9	135
FOT-30b	25.0	60	~0.9	575

(a) Only one set of data obtained - at 11:30 hr.

(b) No laser calibration data. Concentration estimated.

### SMKS Comparison of FO CD Dosage Terms

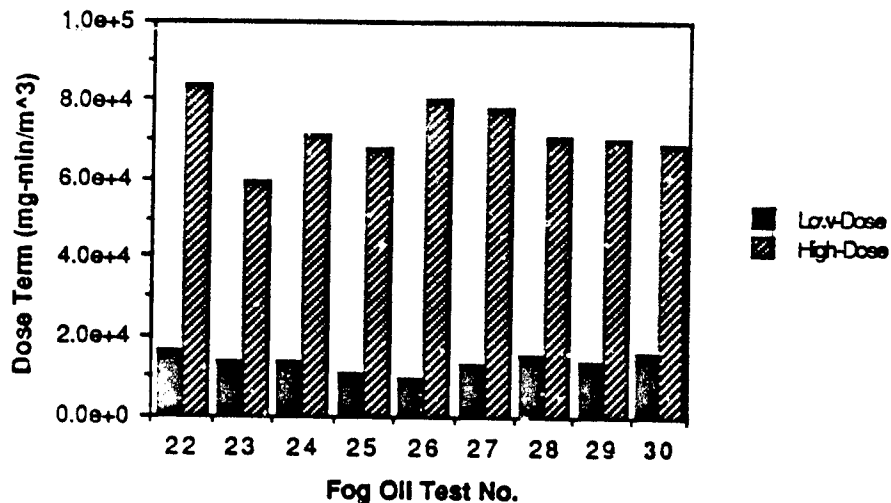


FIGURE 3.7. EXPOSURE DOSE TERMS (mg-min/m<sup>3</sup>) FOR EACH FOG OIL CUMULATIVE DOSE TEST. DOSE TERMS EQUAL THE AVERAGE CONCENTRATION MULTIPLIED BY THE TEST DURATION.

Figure 3.11 shows particle size as influenced by aerosol mass concentration. An increase from 1.8 to 2.8  $\mu\text{m}$  was observed as the aerosol concentration increased from 100 to 550  $\text{mg}/\text{m}^3$ . This increase is equivalent to an increase in the mass or volume of each particle of 3.8 times. A simple theoretical analysis of the relative coagulation potentials for both aerosol concentrations indicated a probable particle volume increase of 3.9 times. The range of particle sizes measured in the present study corresponds with similar data reported by other investigators (Ballou 1981; Katz et al. 1980; Carlon et al. 1977) that have included a MMAD range of 0.6 to 3.0  $\mu\text{m}$ . That the current results were near the upper extreme of this range was probably because the aerosols were aged under simulated field conditions in the wind tunnel and thus were given the opportunity to grow by coagulation.

A lesser effect of ambient humidity on particle size was attributed to the low water content measured on fog oil particles. Very limited data suggest that particle size may have increased from 2.4 to ~2.9  $\mu\text{m}$  (a mass or volume increase of ~1.8 times) as humidity increased from 20% to 64% to 91%. However, measured MMAD values are within the range of particle sizes anticipated based on concentration, and it is possible that no effect of relative humidity on particle size occurred. In contrast, the influence of relative humidity on particle mass of phosphorus aerosols was previously observed to be a greater than 10-times increase at high humidities (Van Voris et al. 1987).

**TABLE 3.4. PARTICLE SIZE DISTRIBUTION FOR FOG OIL AEROSOLS GENERATED WITHIN THE WIND TUNNEL DURING EXPOSURE TESTS**

Test	Relative Humidity (%)	Aerosol Mass Concentration (mg/m <sup>3</sup> )	MMAD (μm)	GSD (-)
<b>Range-Finding</b>				
FOT-4-4	58	780	-	-
FOT-4-8	58	720	1.6	1.7
FOT-5-2	55	690	1.8	1.8
FOT-5-6	52	720	1.9	1.7
<b>Relative Humidity</b>				
FOT-12	20	730	2.4	1.7
FOT-14	64	740	3.0	1.7
FOT-15	91	830	2.8	1.6
FOT-18	74	810	2.7	1.7
FOT-16(dry)	61	870	-	-
FOT-16(rain)	88	760	-	-
<b>Wind Speed</b>				
FOT-17	66	910	-	-
FOT-18	72(a)	940	-	-
FOT-19	62	990	-	-
FOT-20	58	960	-	-
<b>Cumulative Dose</b>				
FOT-22a	59	68(b)	~1.8	1.8
FOT-22b	61	350(b)	2.4	1.5
FOT-23a	59	110	2.0	1.6
FOT-23b	60	495	3.0	1.6
FOT-24a	62	113	1.6	1.7
FOT-24b	58	395	2.7	1.7
FOT-25a	64	73	-	-
FOT-25b	60	~560	3.1	1.7
FOT-26a	61	80	-	-
FOT-26b	56	670	2.9	1.7
FOT-27a	61	108	2.1	1.6
FOT-27b	58	645	-	-
FOT-28a	58	130	1.8	1.6
FOT-28b	56	645	2.6	1.7
FOT-29a	63	110	1.8	1.6
FOT-29b	60	585	2.9	1.7
FOT-30a	63	135	1.8	1.7
FOT-30b	60	575	2.6	1.7

(a) Only one set of data obtained - at 11:30 hr.

(b) No laser calibration data. Concentration estimated.

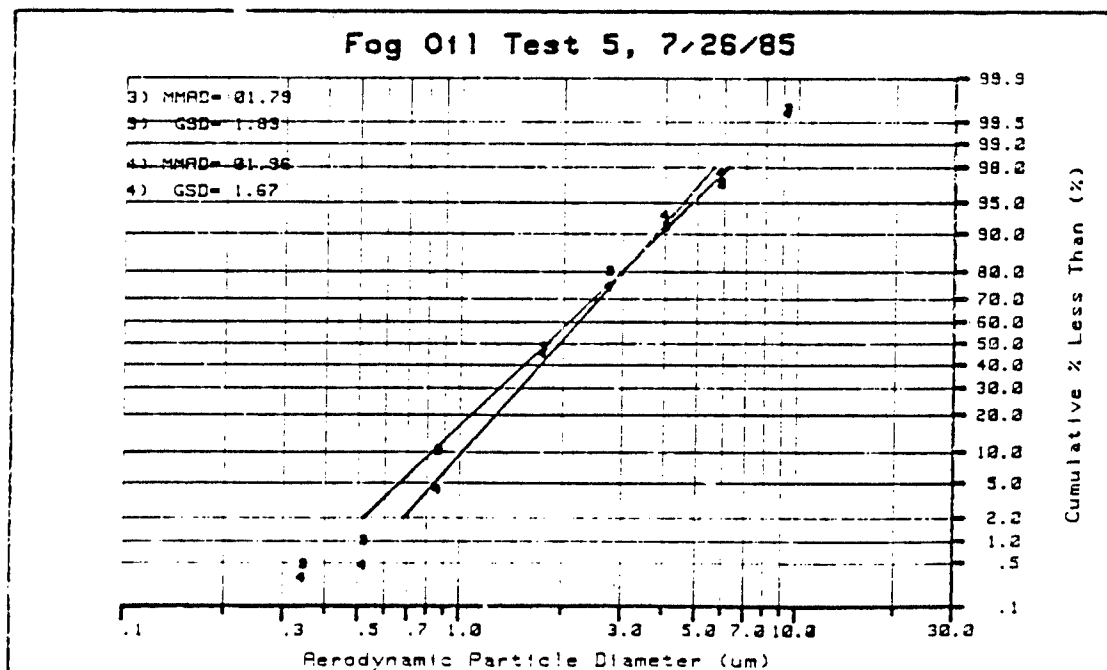
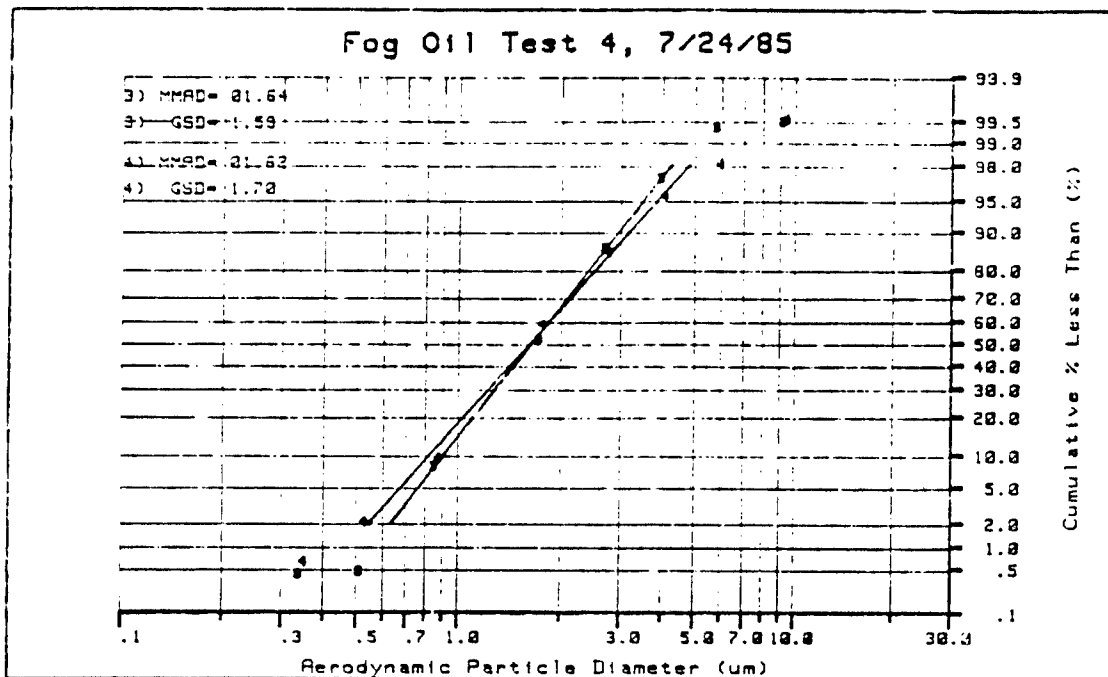


FIGURE 3.8. PARTICLE SIZE DISTRIBUTIONS MEASURED DURING THE FOG OIL RANGE-FINDING TEST SERIES

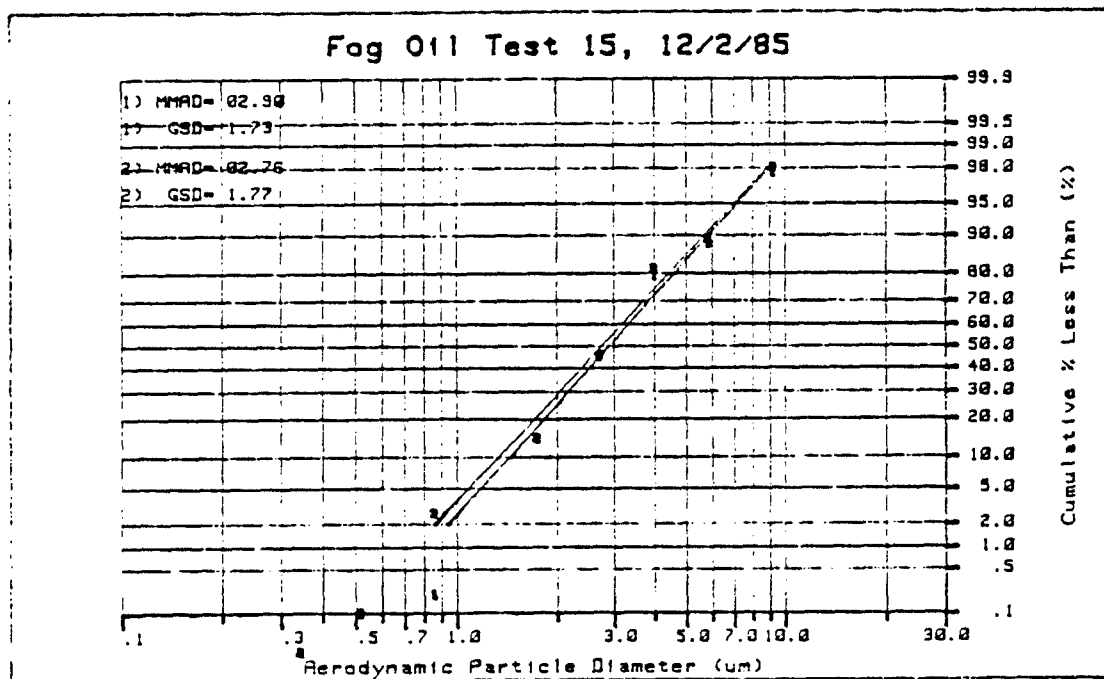
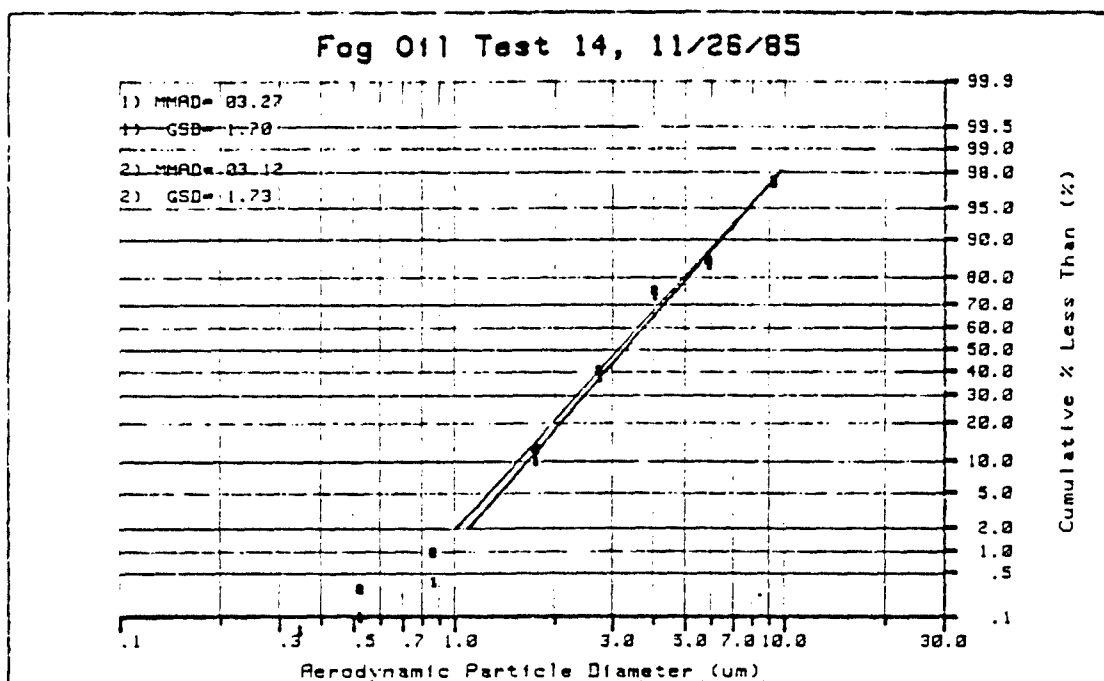


FIGURE 3.9. PARTICLE SIZE DISTRIBUTIONS MEASURED DURING THE FOG OIL RELATIVE HUMIDITY TEST SERIES

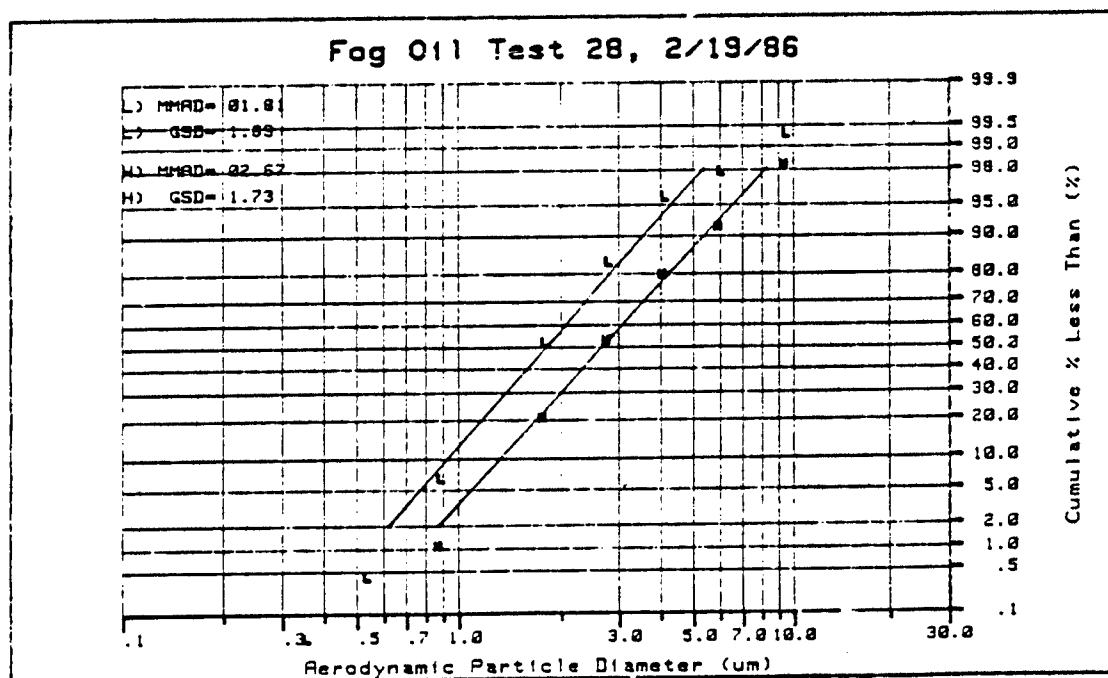
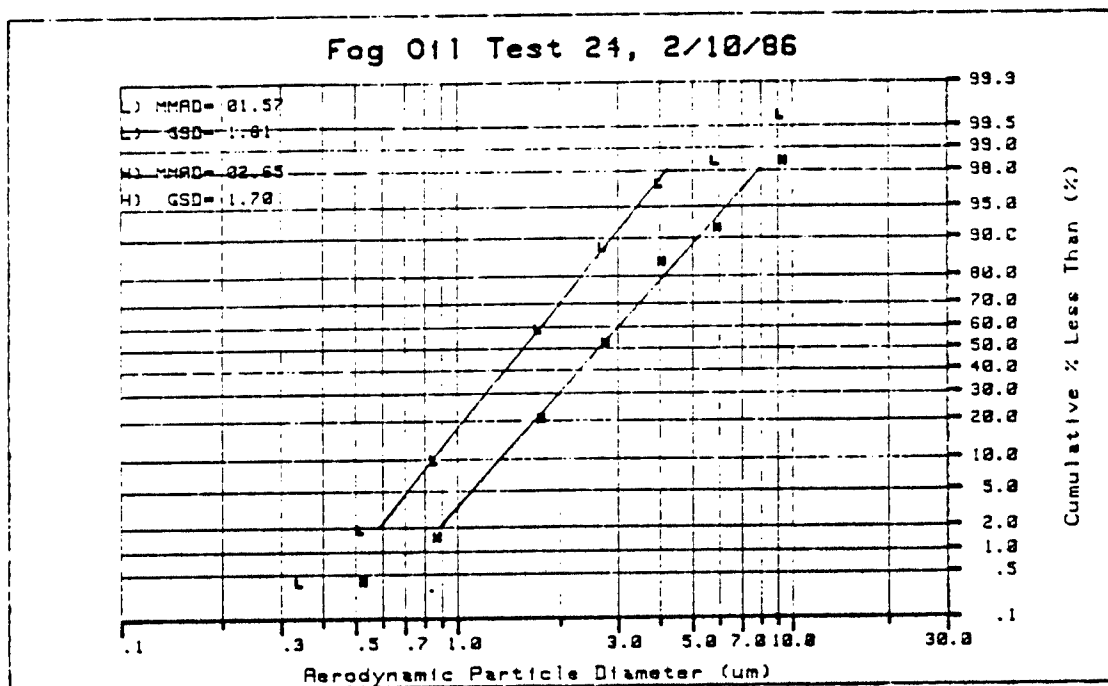


FIGURE 3.10. PARTICLE SIZE DISTRIBUTIONS MEASURED DURING THE FOG OIL CUMULATIVE DOSE TEST SERIES



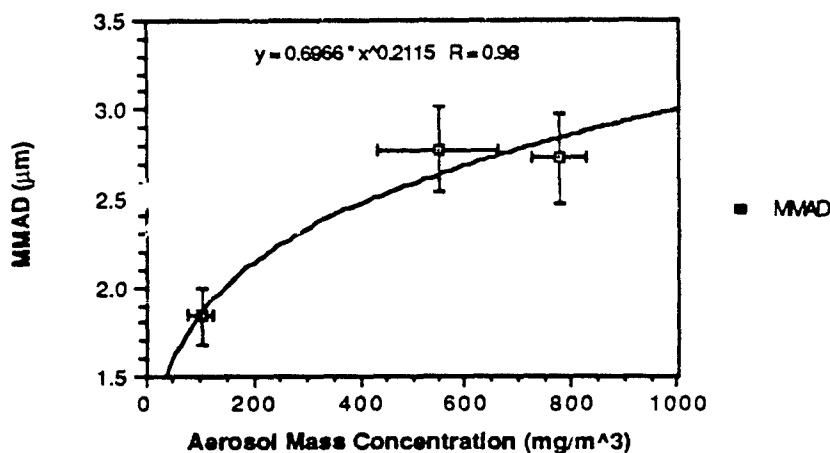


FIGURE 3.11. INFLUENCE OF AEROSOL MASS CONCENTRATION ON PARTICLE SIZE DISTRIBUTION OF FOG OIL AEROSOLS

The smaller size of the fog oil particles in the range-finding tests was attributed to a greater than 20-cfm air transfer rate between the laboratory and wind tunnel. The wind tunnel was slightly modified after the range-finding tests to provide better control over the aging of obscurant aerosols.

The effect of condensation of water vapor to fog oil particles was seen to be limited, and was probably affected by the insoluble composition of the fog oil. The actual mass of particulate material collected on filter samples was compared to the desiccated, or non-aqueous particulate mass (desiccation period of 1 day to 6 days). For relative humidities ranging from 20 to 91%, the ratio of actual particulate mass to desiccated particulate mass varied between 0.92 and 1.00. The lower ratios were obtained after desiccation of 4 days or 6 days, and were determined to primarily reflect evaporation of components of the fog oil and not to be related to an actual increase of the water fraction of the particulate mass. Seven fog oil aerosol samples collected during test FOT-15 (91% RH) were desiccated for only 1 day, and resulted in a desiccated-to-actual mass ratio of  $0.99 \pm 0.02$  (one standard deviation).

The evaporation of fog oil from an aerosol sample was measured periodically over a 2-month period. This was done to provide comparison with depuration measurements of fog oil from plant and soil surfaces. Fog oil was collected by deposition to six 47-mm glass fiber filters during an exposure test and then allowed to evaporate. Three filters were placed into a desiccator (drierite) and three filters were allowed to air dry. No difference was observed in the

evaporation rate of fog oil between the two methods. Figure 3.12 shows the results of these measurements; uncertainty in the figure represents the standard deviation of the six samples. Approximately 14% of the fog oil mass was observed to have volatilized after a drying period of 65 days.

### 3.2.2 Mass Loading and Deposition Velocity to Surrogate Surfaces

The deposition velocity of fog oil aerosol to surrogate surfaces was measured during selected cumulative dose tests to provide comparison with deposition to plant and soil surfaces. Three or four 47-mm glass fiber filter substrates were suspended in the wind tunnel test section just upwind of the plant canopy. The filters were suspended on springs so that they were flat and oriented horizontally. Deposition occurred primarily on the upwind edge and on the flat top of the filters. The rate of deposition to the filters, or the deposition velocity, was calculated as the filter mass load divided by the product of the air concentration, substrate area, and the time of exposure, and has dimensions of length per time, or cm/s. The area used in the calculations ( $34 \text{ cm}^2$ ) included both the upper and lower surfaces of the filter less the area attached to the spring. Table 3.5 provides a summary of the deposition velocity results. Under the cumulative dose test conditions, the deposition velocity of fog oil particles to the surrogate surfaces averaged  $0.027 \pm 0.003 \text{ cm/s}$ .

### 3.3 MASS LOADING AND DEPOSITION VELOCITY TO RECEPTOR SURFACES

The mode of evaluation currently being employed provides a range of generally important and measurable parameters [RH, wind speed, temperature, deposition velocity (Vd), and mass loading (ML)] which can be readily applied to the field environment for projection of smoke related damage. The primary value of the ML data is as a reference point in evaluating the influence of treatment variables on toxicity, and intercomparisons of smoke effects. Deposition velocities are used in the obscurant smoke studies to allow evaluation of foliar collection efficiency based on plant species, and for predictive purposes, since this parameter can be employed to normalize the air concentration/exposure duration variable inherent in mass loading data and provide a basis for projecting potential field effects. In the latter instance, the experimentally determined Vd value can be employed to determine dose to foliage based on a range of field exposure scenarios.

#### 3.3.1 Range-Finding Test Series

Aerosol characteristics for the RFT-FO exposures have been presented in Table 3.3. Average airborne FO concentrations for the four treatments were  $737 \pm 40 \text{ mg FO/m}^3$ . Mass

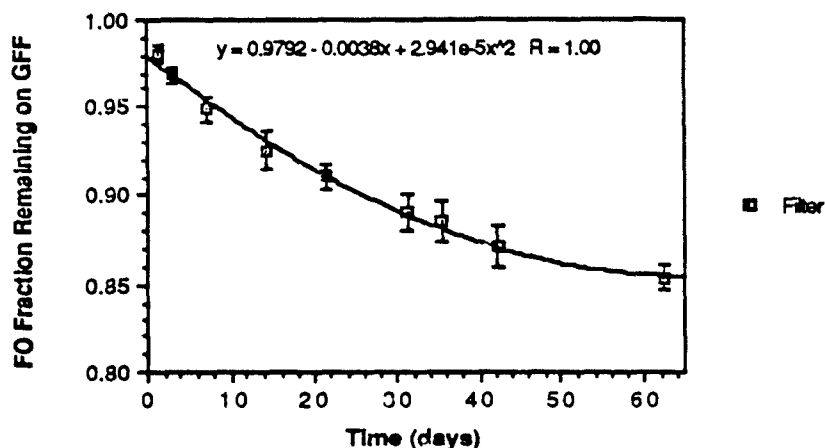


FIGURE 3.12. EVAPORATION OF FOG OIL AEROSOL DEPOSITED TO 47-mm GLASS FIBER FILTER SUBSTRATE. SIX SAMPLES WERE AIR DRIED OR DESICCATED FOLLOWING PARTICLE DEPOSITION DURING FOT-31.

TABLE 3.5. DEPOSITION VELOCITIES OF FOG OIL AEROSOLS TO SURROGATE GLASS FIBER FILTER SUBSTRATE SUSPENDED IN THE WIND TUNNEL TEST SECTION

Test	Wind Speed (m/s)	Surrogate Surface Deposition Velocity (cm/s)
Cumulative Dose		
FOT-25b	0.90	0.024 ± 0.003
FOT-26b	0.86	0.030 ± 0.004
FOT-27b	~0.9	0.026 ± 0.003
FOT-30b	~0.9	0.029 ± 0.006

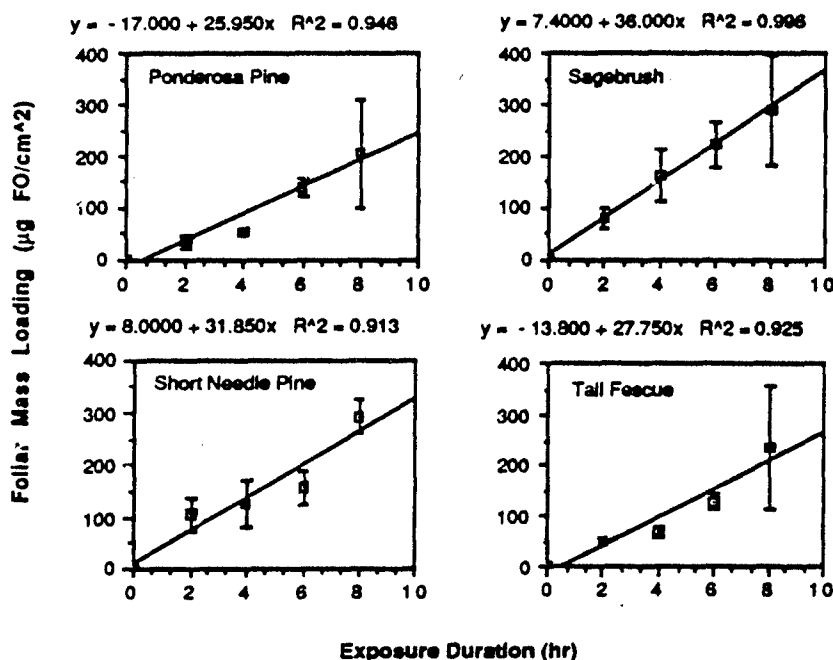
loading rates were determined for ponderosa pine, short needle pine, sagebrush and tall fescue following 2-, 4-, 6-, and 8-hr exposure. These are shown in Table 3.6, along with the air concentrations for the four exposures. Overall, ML values range from 30 to 300  $\mu\text{g FO}/\text{cm}^2$  foliage. While ML value increases with increased exposure time within each canopy type, the incremented increases are not proportional to exposure duration for each plant species. The relationship between exposure duration and ML is shown in Figure 3.13. The lack of linearity in deposition for the pines and grass is generally contrary to the results for the phosphorus smokes (Van Voris et al. 1987). Differences are also seen between canopy types, where sagebrush generally exhibits higher ML levels than the other three species. Substantial

**TABLE 3.6. MASS LOADING OF FOG OIL SMOKES TO FOLIAR SURFACES AS A FUNCTION OF EXPOSURE DURATION**

Plant Species	Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ foliage)(a)			
	Exposure Duration (hr)(b)			
	2	4	6	8
Ponderosa Pine	$33 \pm 13$	$55 \pm 7$	$140 \pm 16$	$206 \pm 105$
Short Needle Pine	$104 \pm 33$	$124 \pm 45$	$157 \pm 32$	$292 \pm 31$
Sagebrush	$82 \pm 19$	$163 \pm 53$	$222 \pm 44$	$290 \pm 106$
Tall Fescue	$50 \pm 6$	$69 \pm 10$	$129 \pm 15$	$238 \pm 120$

(a) Mass loading calculated based on 2 times the projected area. Avg  $\pm$  s.d., n=12.

(b) Air concentrations for the 2-, 4-, 6-, and 8-hr treatments were 690, 780, 760, and 720  $\text{mg FO}/\text{m}^3$ , respectively.



**FIGURE 3.13. PLOT OF MASS LOADING TO FOLIAR SURFACES VERSUS EXPOSURE DURATION**

differences are also seen in ML levels for the two pine species. The significance of these differences cannot be assessed from this single data set. Much of the fog oil data has an unexpectedly high variability with respect to ML and associated parameters; this may be due to its relatively high volatility and subsequent loss from the receptor surfaces. This aspect will be discussed in Section 3.4.

Values of  $V_d$  based on plant type and exposure duration are shown in Table 3.7. Overall the calculated values, within each treatment set (exposure duration), are much more variable than reported for the phosphorus smokes. Ideally,  $V_d$  values should be independent of exposure duration and constant for each plant species in this study. The lack of consistency may lie in the fact that the MMAD of fog oil particles in these studies was approximately 1.7  $\mu\text{m}$ , compared with 0.75  $\mu\text{m}$  for the phosphorus smokes. This could affect the mode and patterns of deposition within each canopy type. Alternatively, variations may be due to the volatility of fog oil residues, with evaporative losses being more significant at the ML associated with the 2- and 4-hr exposures. These  $V_d$  values also tend to explain the basis of the noted non-linearity in mass loading levels with exposure duration. However, it should be noted that this inconsistency in  $V_d$  is not unacceptable, since we still only have a factor of two difference within plant treatments. The average  $V_d$  value for fog oil, for each species, ranges from 7.5 to 14.6  $\times 10^{-3}$  cm/sec. This is substantially similar to values obtained for red phosphorus in the RFT (11 to 13  $\times 10^{-3}$  cm/sec), under similar delivery conditions.

### 3.3.2 Relative Humidity Test Series

The purpose of the RHT series is to assess the impact of atmospheric moisture (RH) on interception efficiency ( $V_d$ ) of different types of plant canopies for individual obscurant smokes by determining: 1) the effect of moisture on smoke phytotoxicity and its correlation with dose (ML), 2) whether adverse plant effects are ameliorated or intensified as a result of precipitation events (rainout or post-exposure leaching) and, 3) the correlation of the level of smoke, or dose, with near- and long-term environmental damage.

While there was a measurable change in the physical and chemical behavior of the hygroscopic phosphorus smokes with relative humidity (Van Voris et al. 1987), there appears to be little consistent effect of RH on fog oil aerosols and foliar deposition, as shown in Table 3.8 and Figure 3.14. There is no statistically significant difference in ML levels for fog oil deposited to foliage of short needle pine, sagebrush, and tall fescue at RH's of 20, 64 and 91%. This would suggest that particle growth during aerosol aging, thus the particle size of fog oil smokes is not affected by RH. There is some indication that RH affects the ML of fog oil to canopies of ponderosa pine and bush bean based on comparison to the 20% RH treatment.

**TABLE 3.7. CALCULATED DEPOSITION VELOCITIES FOR AIRBORNE FOG OIL SMOKES TO FOLIAR SURFACES AS A FUNCTION OF EXPOSURE DURATION**

Plant Species	Vd (cm/sec x 10 <sup>3</sup> ) Exposure Duration (hr)(a)				Species Average(b)
	2	4	6	8	
Ponderosa Pine	6.6	4.9	8.5	9.9	7.5 ± 2.2
Short Needle Pine	20.9	11.0	9.6	14.1	13.9 ± 5.0
Sagebrush	16.5	14.5	13.5	14.0	14.6 ± 1.3
Tall Fescue	10.1	6.1	7.8	11.5	8.9 ± 2.3

(a) Air concentrations for the 2-, 4-, 6-, and 8-hr treatments were 690, 780, 760, and 720 mg FO/m<sup>3</sup>, respectively. 2 ML calculated based on 2 times the projected area.

(b) Avg ± s.d., n=12.

**TABLE 3.8. MASS LOADING OF FOG OIL (SGF-2) SMOKES TO FOLIAR SURFACES AS A FUNCTION OF RELATIVE HUMIDITY AND RAINOUT (RHT). EXPOSURES WERE CONDUCTED FOR 4 HR, AT 2 MPH(a)(b).**

Plant Species	Mass Loading (µg FO/cm <sup>2</sup> foliage)(c)			
	Relative Humidity (%)			Rainout
	20	64	91	
Ponderosa Pine	282 ± 115	544 ± 107 ++	567 ± 221 +	425 ± 69 -
Short Needle Pine	348 ± 104	544 ± 227 -	649 ± 426 -	539 ± 101 -
Sagebrush	570 ± 223	490 ± 93 -	469 ± 90 -	610 ± 111 -
Tall Fescue	239 ± 70	401 ± 109 -	320 ± 69 -	377 ± 173 -
Bush Bean	136 ± 25	257 ± 71 ++	207 ± 82 -	140 ± 23 -

(a) Mass loading levels for the 20, 64, 91% and rainout treatments are based on air concentration of 730, 740, 830 and approximately 810 mg/m<sup>3</sup>, respectively; mass loading is calculated using 2 x the projected leaf area. The rainout study involved 2-hr smoke exposure, followed by 2-hr exposure to aerosol in the presence of a simulated rainfall of approximately 1 cm/hr.

(b) Aerosol MMAD (1GSD) for the 20, 64, and 91% RH treatments were 2.4 (1.7), 3.0 (1.7) and 2.8 (1.6) µm, respectively.

(c) Avg ± s.d., n=10; Student t-test, P≤0.05(++), P≤0.1(+), not significant (-).

However, between plant species, there appears to be a difference in interception efficiency between the closed canopies of bush bean and tall fescue, compared with the open canopies of the pines and sagebrush (P≤0.01). This difference, or reduced ML to bush bean, was also observed with the phosphorus smokes.

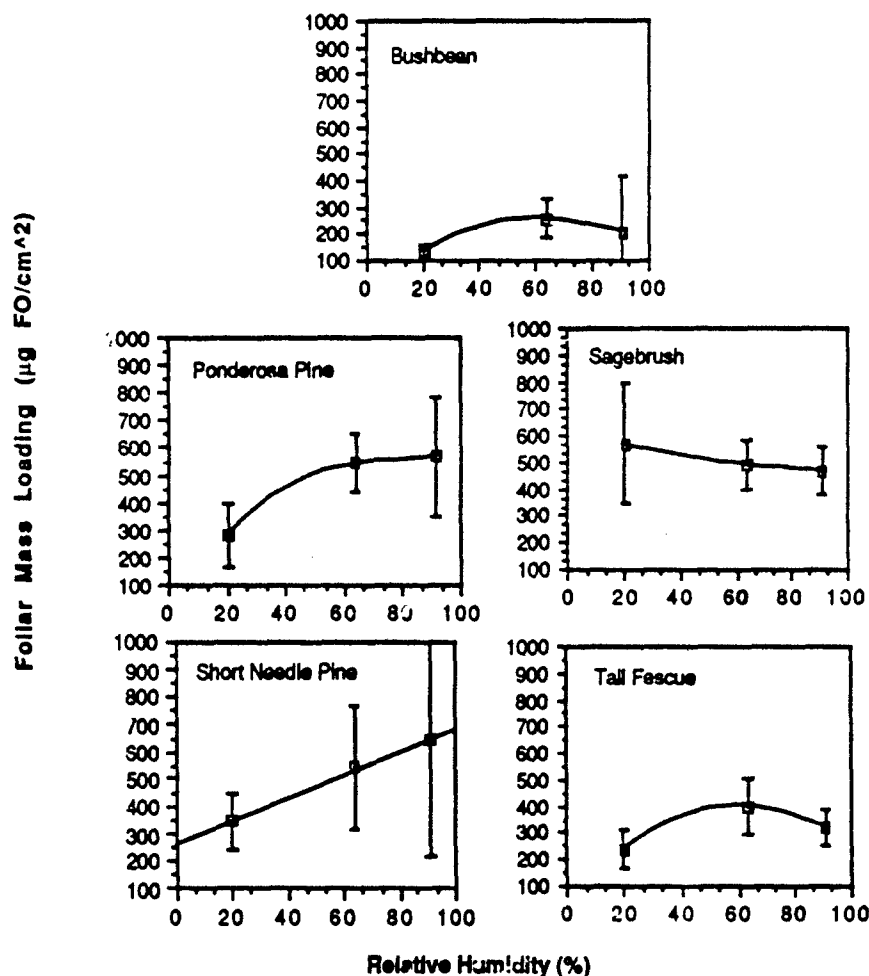


FIGURE 3.14. INFLUENCE OF RELATIVE HUMIDITY ON FOLIAR MASS LOADING

One additional treatment was employed in the RHT, namely, the effect of a simulated rainout during exposure on ML. This involved exposure of plants to fog oil smokes for 2 hr, followed by application of a simulated rainfall of approximately 0.5 in. for an additional 2 hr during fog oil exposure. Surprisingly, there was no significant reduction in ML to any of the plant species when compared with the 91% RH, 4-hr exposure in the absence of the rainout. Apparently fog oil, unlike the phosphorus smokes, is not displaced from the foliage by displacement or as an emulsion. It is also likely that the fog oil hydrocarbons readily dissolve into the waxy cuticles of the leaf surfaces and become physically unavailable for displacement.

The mass loading data indicated that RH had only a slight influence on foliar collection efficiency or deposition; however, these results can be biased by differences in both particle size and air concentrations between treatments or generation runs. Although there is no convenient means to compensate for changes in particle size, differences in air concentration between exposures can be normalized by use of Vd to compare collection efficiency of the various canopy types. Table 3.9 provides the calculated Vd values for the four treatments. Based on these values, it would appear that there is no consistent effect of RH on collection efficiency for the various canopy configurations except for a slightly significant increase in Vd for the pines and bush bean between 20% and 64% RH. The reduced Vd for tall fescue and bush bean are statistically lower ( $P \leq 0.05$ ) than for the pines and sagebrush for all treatments except for 20% RH. Although calculation of a Vd value for the rainout study would normally be inappropriate, it has been provided to point out the general lack of leaching/washoff from foliage ( $P \geq 0.1$ ) under simulated rainfall conditions. Differences in aerosol size and distribution (Table 3.8) should not influence the above observations significantly, particularly since the MMAD of particles at 20% RH (2.4) is lower than that for 64 and 91% RH (3.0 and 2.8). This difference in MMAD would, if anything, slightly reduce Vd values for the low humidity treatment.

In summary, Vd values (interception efficiency) for fog oil deposition from the air column to plant surfaces indicated no dramatic effect of RH on interception by individual plant species. This would generally be expected for fog oils as compared with water soluble smokes such as red and white phosphorus. However, there was a difference in Vd between species. The pines and sagebrush exhibited the highest Vd values, ranging from 0.030 to 0.050 cm/sec. Values for tall fescue and bush bean averaged 0.018 to 0.030 cm/sec. The Vd values for fog oil are approximately a factor of 8 higher than for the phosphorus smokes, and result from the larger particle size of fog oil smokes (see footnote, Table 3.8).

In addition, fog oil mass loading is higher for the more open canopy structures of the pines and sagebrush, compared with the closed canopy characteristic of broadleaf plants like bush bean and tall fescue. It is interesting to note that during the rainout study, ML levels (at 92% RH) are comparable to those obtained in the absence of a simulated rainfall (Table 3.9). This indicates that fog oil deposited to leaves is not subject to removal by precipitation events. More importantly, fog oil deposition apparently continues in the presence of a rainfall event. A similar behavior was noted during the post-exposure simulated rainfall, in that fog oil ML values for all plants and treatments within a test series were statistically similar prior to and following leaching (Table 3.10).



**TABLE 3.9. CALCULATED DEPOSITION VELOCITIES FOR AIRBORNE FOG OIL SMOKES TO FOLIAR SURFACES AS A FUNCTION OF RELATIVE HUMIDITY AND RAINOUT (RHT)**

Plant Species	Deposition Velocity Vd (cm/sec x 10 <sup>3</sup> )(a)			
	Relative Humidity (%)			Rainout
	20	64	91	
Ponderosa Pine	27 ± 11	51 ± 5 ++	47 ± 18 +	36 ± 6 -
Short Needle Pine	33 ± 10	50 ± 21 +	41 ± 24 -	46 ± 8 -
Sagebrush	53 ± 21	45 ± 8 -	39 ± 7 -	52 ± 9 -
Tall Fescue	23 ± 6	37 ± 10 -	27 ± 6 -	27 ± 8 -
Bush Bean	13 ± 2	24 ± 6 +	17 ± 7 -	12 ± 2 -

(a) Avg ± s.d., n=10; Student t-test, P≤0.05(++), P≤0.1(+), not significant (-).

**TABLE 3.10. INFLUENCE OF POST-EXPOSURE SIMULATED RAINFALL ON RETENTION OF FOLIARLY DEPOSITED FOG OIL**

Test Series	Foliar Retention (% of pretreatment value)(a)
Range Finding Test	98 ± 11
Relative Humidity Test	102 ± 5
Wind Speed Test	95 ± 12

(a) Avg ± s.d., n = 36.

### 3.3.3 Wind Speed Test Series

The purpose of the WST series is to determine the influence of wind speed on Vd and ML for different types of plant canopies. Because of the increased deposition that occurs at higher wind speeds, this study provides an opportunity to evaluate plant toxicity responses to a wider range of dose levels. Deposition velocity data for air to plant foliage are presented in Table 3.11 and Figure 3.15. Results are qualitatively similar to those observed with the phosphorus smokes with increased deposition of fog oil to plant canopies as wind speed increases. Values of Vd for ponderosa pine and sagebrush increase rapidly at around 6 mph.

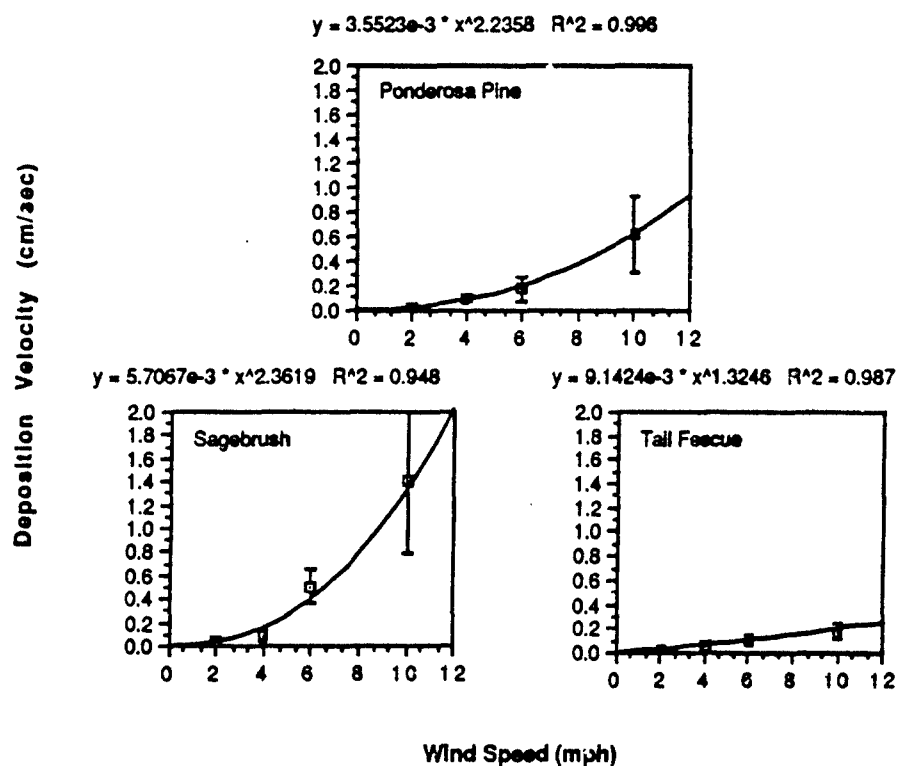
**TABLE 3.11. CALCULATED DEPOSITION VELOCITIES FOR AIRBORNE FOG OIL SMOKES TO FOLIAR SURFACES AS A FUNCTION OF WIND SPEED (WST)(a)(b)**

Species	Deposition Velocity Vd (cm/sec x 10 <sup>3</sup> )(c)			
	Wind Speed (mph)			
	2	4	6	10
Ponderosa Pine	16 ± 6	90 ± 42	177 ± 99	617 ± 316
Sagebrush	37 ± 10	87 ± 44	507 ± 144	1398 ± 607
Tall Fescue	21 ± 7	65 ± 8	103 ± 47	177 ± 60

(a) Exposures conducted for 1-hr (45 min for the 10-mph treatment) at a RH of 58 to 72%.

(b) Fog oil air concentration for the 2, 4, 6, and 10 mph exposures were 910, 990, 960, and 940 mg/m<sup>3</sup>.

(c) Mass loading values used to compute Vd were based on 2 x the projected foliar area.



**FIGURE 3.15. RESPONSE OF DEPOSITION VELOCITY TO INCREASING WIND SPEED**

This rapid rise in  $V_d$  is not observed with tall fescue. Deposition velocities between 2 and 10 mph increase by a factor of 38 for the pine and sagebrush, and by a factor of 8 for tall fescue. The increase in  $V_d$  for tall fescue is substantially less than that observed with the blando brome employed in the phosphorus smoke studies. This may result from the comparatively low canopy density of fescue when compared with the denser canopies characteristic of ponderosa pine, sagebrush, and blando brome.

The logarithmic increase in  $V_d$  with increasing wind speed may be the most critical factor in projecting field impacts from fog oil. These results indicate that as wind speed increases, particularly beyond 6 mph, deposition and thus dose to foliar surfaces increase markedly.

Foliar ML values for the three plant species employed in the WST are given in Table 3.12. Dose levels for ponderosa pine increase from 47 to 1400 mg FO/cm<sup>2</sup> for foliage, from 129 to 3400 for sagebrush, and from 70 to 450 for tall fescue. These 1-hr dose levels bracket those from the 4-hr RHT exposures. The ML levels show the rapid rise in loading at approximately 6 mph seen with the computed  $V_d$  values. As in the RHT series, post-exposure leaching had no significant effect on foliar loading levels.

### 3.4 RESIDENCE TIME OF FOG OIL ON SOIL AND PLANT SURFACES

Early in the fog oil studies, there was an indication that fog oil constituents were being rapidly lost from filter and foliage samples, most likely due to volatilization of low molecular weight components. This resulted in some modification of collection and chemical stabilization procedures for samples, and initiation of a set of brief studies to quantitate losses due to volatilization of fog oil components.

#### 3.4.1 Residence Time of Fog Oil on Foliar Surfaces

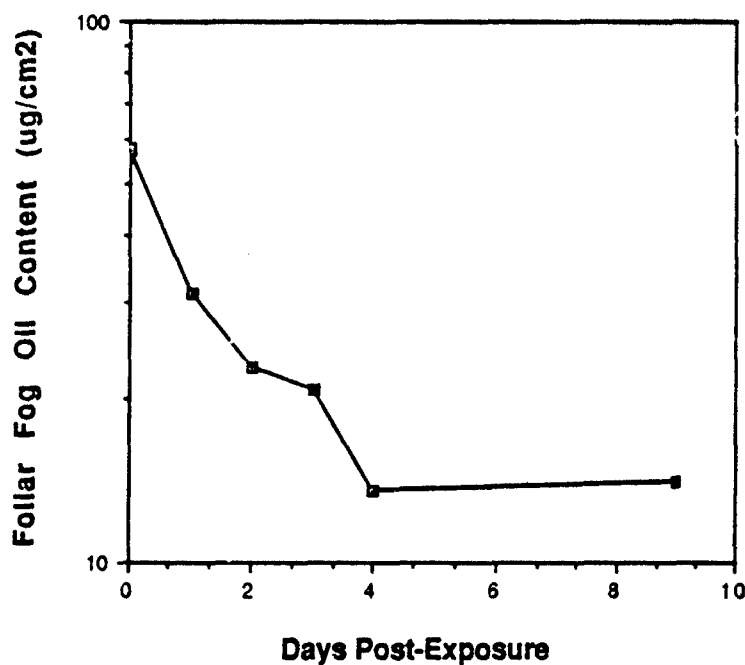
As part of the CDT series, several plants were exposed to fog oil smokes for 4 hr, and foliar samples analyzed to resolve the persistence of fog oil. Figure 3.16 shows the losses of total fog oil from pine needles over a 9-day period. From log/linear plots of these results it appears that the depuration curve has two components. The first accounts for the rapid loss of fog oil, and has a half-time of 1.7 days. The second component has an extended half-time. It should be noted that the background hydrocarbon content of these needles is approximately 7 µg/cm<sup>2</sup>, and therefore, over the 9-day period the fog oil content of foliage is reduced from 58 to 12 µg FO/cm<sup>2</sup>. This represents an 80% reduction in dose. No estimates are available as to the fraction of the foliar dose which is absorbed into the plant and not available for extraction.

**TABLE 3.12. MASS LOADING OF FOG OIL SMOKES TO FOLIAR SURFACES AS A FUNCTION OF WIND SPEED (WST)**

Species	Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ foliage) (a)			
	Wind Speed (mph)			
	2	4	6	10
Ponderosa Pine	$47 \pm 16$	$305 \pm 145$	$571 \pm 321$	$1366 \pm 859$
Sagebrush	$129 \pm 29$	$308 \pm 161$	$1695 \pm 448$	$3383 \pm 1450$
Tall Fescue	$70 \pm 23$	$163 \pm 50$	$321 \pm 145$	$450 \pm 153$

(a) Mass loading values used to compute  $V_d$  were based on 2 x the projected foliar area. Exposure duration for the 10 mph treatment was 45 min.

**Depuration of Fog Oil Deposited to Foliage of Ponderosa Pine**



**FIGURE 3.16. PERSISTENCE OF FOG OIL CONSTITUENTS ON FOLIAR SURFACES OF PONDEROSA PINE. PLANTS EXPOSED TO FOG OIL SMOKES FOR 4 HR, TRANSFERRED TO CONTROLLED ENVIRONMENT CHAMBERS, AND SAMPLES OF FOLIAGE ANALYZED FOR RESIDUAL FOG OIL OVER 9 DAYS.**

### 3.4.2 Residence Time of Fog Oil on Soil Surfaces

Soils contaminated with fog oil smokes were maintained in controlled environment chambers, and soil cores removed periodically for analysis over a 42-day period. Results for the Maxey Flats soil are shown in Figure 3.17.

From the log plots it is clearly seen that fog oil is lost from each of the three exposure treatments. Again two loss components are evident. The first has a half-time of approximately 20 days, the second a half-time of approximately 500 days, although the latter half-time may not be a reliable estimate because of the short duration of the study.

A similar data set for Burbank soil is shown in Figure 3.18. In the case of the Burbank sandy-loam, depuration of fog oil due to volatilization does not exhibit a two component loss as observed for Maxey Flats soil. The overall half-life of fog oil is calculated at approximately 60 days for the Burbank soil. This is a substantially lower rate of depuration than for the Maxey silty-clay soil. This is surprising since the clay is much more compact and less aerated than the sandy soil. However, while losses appear to be near minimal in the clay soil at 20 days, losses appear to continue unattenuated after 42 days in the sandy soil.

From the data presented and the half-lives calculated for the persistence of fog oil on the two soils, a hypothesis based on physical soil characteristics can be proposed. It is possible that the "fast" volatilization of fog oil from Maxey Flats soil may be from external surfaces of this relatively porous soil, followed by "slow" diffusion-limited volatilization from internal capillary pores, i.e., the extremely long half-life component. The Burbank soil, having a very small percentage of capillary type pores, has lower total porosity and surface area, and is dominated by volatilization from relatively large pore spaces. This rate of loss would not be as "fast" as volatilization from large external surfaces found in Maxey Flats, and not so "slow" as that limited by diffusion.

### 3.5 PHYTOTOXICITY OF FOG OIL DEPOSITED TO FOLIAR SURFACES

The phytotoxicity of fog oil smokes was evaluated for direct contact toxicity following contamination of foliar surfaces, residual effects of foliar contact on regrowth in a perennial grass, and indirect effects of soil-deposited smokes on germination and growth of grass. The Range Finding, Cumulative Dose, Relative Humidity, and Wind Speed test series provide a means to evaluate smoke effects responses to variables including exposure duration, intermittent accumulated doses, relative humidity and rainout, and wind speed. In addition, in two of the experiments, the ameliorating effect of post-exposure simulated rainfall was

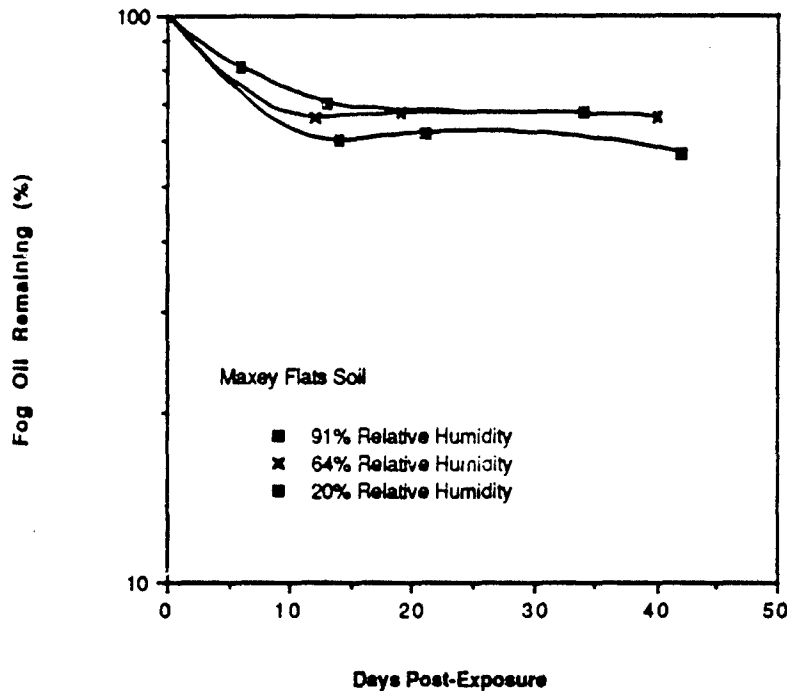


FIGURE 3.17. PERSISTENCE OF FOG OIL COMPONENTS IN MAXEY FLATS CLAY SOIL. SOILS WERE EXPOSED FOR 4-HR TO SMOKES DELIVERED AT 20%, 64%, AND 91% RELATIVE HUMIDITY.

evaluated. The latter can either reduce adverse effects by reducing mass loading levels, or accentuate the effect of a particular smoke by increasing solubility and absorption of toxic components of the deposited smoke.

The direct effects of fog oil smokes were studied, for a series of foliage types, with respect to both dose and the influence of environmental parameters on observed toxicity. Direct effects are basically those that result from accumulation of smoke residues on the surfaces of plant canopies. Adverse effects, if present, can be induced by disruption of any number of plant processes. These include simple osmotic effects, pH effects, membrane disruption or a range of toxicity responses to specific ions or compounds. Foliar contact with smokes can also include, for example, residual impacts resulting from smoke components being absorbed through the foliage and transported to roots, and result in a residual or later effect (i.e., grass regrowth, residual effects studies).

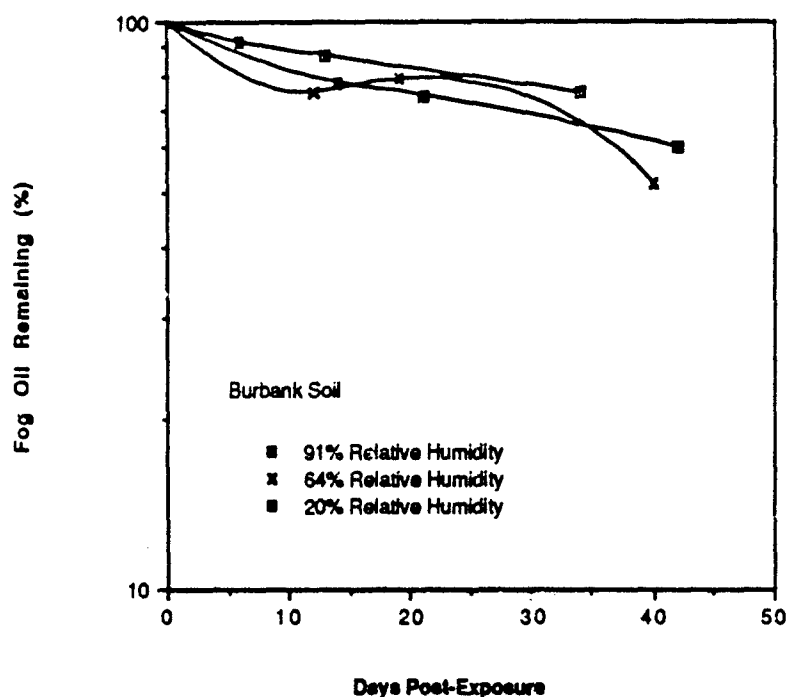


FIGURE 3.18. PERSISTENCE OF FOG OIL COMPONENTS IN BURBANK SANDY-LOAM SOIL. SOILS WERE EXPOSED FOR 4 HR TO SMOKES DELIVERED AT 20%, 64%, AND 91% RELATIVE HUMIDITY.

In three of the experiments biomass production resulting from grass regrowth was evaluated. Biomass production can be used to evaluate any long-term residual effects from direct foliar contamination, and assumes that if residual effects are to appear, that they result from transport of persistent residues to the root. In practice the exposed grass is observed for 2 wk following exposure, cut back, and allowed to regrow for 4 to 6 wk. Any changes in either dry matter production and/or growth characteristics, compared with the controls, is indicative of a residual effect.

In addition to direct and residual effects, the indirect effects of obscurant smoke deposition to soils and subsequent effects on plant growth were evaluated. These indirect effects include germination, dry matter production, and general toxicity responses, if present. These studies employed only a single grass species. The deposition of smokes to soil

surfaces can, in some instances, change soil characteristics sufficiently to affect plant growth and vigor (indirect effects). For example, acidic smokes, such as phosphorus and HC, can cause desorption of soil-immobilized elements, making them more available for plant uptake and cause subsequent ion imbalances (P, Zn), or in the case of HC, increase the soil loads of Zn with the same result. Smokes such as fog oil can alter the aeration, physical characteristics, and base metabolism of soils with a resulting adverse plant effect. These are only a few of the potentially adverse aspects of smoke accumulation in soils.

As noted previously, the evaluation of toxicity responses for intercomparison purposes is of little value if a common denominator is not present. In all of the toxicity studies the point of reference was the mass loading value or exposure level. The mass loading rate was determined by chemical measurement of the amount of smoke deposited to a unit area or weight of foliage and is an absolute index of dose. For the fog oil exposures, total hydrocarbons deposited were quantitated, using relatively rapid HPLC procedures. Phenotypic toxicity responses to fog oil smokes are based on a modified Daubenmire scale and are provided in Table 2.4.

### 3.5.1 Direct Foliar Contact Toxicity

Range Finding Test Contact Toxicity. The Range Finding Test (RFT) involved exposure of the five plant test species to fog oil smokes of approximately  $800 \text{ mg/m}^3$ , for 2, 4, 6, and 8 hr. Wind speed was maintained at 2 mph, and RH at 25%. Plants exposed to fog oil for 2, 4, 6 and 8 hr received doses (mass loading values and exposure conditions were provided in Table 3.6) ranging from 33 to  $290 \mu\text{g FO/cm}^2$  foliage. Loading rates to short needle pine and sagebrush were substantially higher than for ponderosa pine and tall fescue. Based on the mass loading values for individual treatments and plant species, the progression and intensity of phytotoxic responses to fog oil are shown in Table 3.13.

Overall, based on mass loading rates and toxicity responses (Figure 3.19), ponderosa pine and sagebrush were substantially more resistant to damage from exposure to fog oil than were short needle pine and tall fescue. Also, older growth appears to be more susceptible to damage than new or younger growth, and stabilization of symptoms was generally delayed for a period of time (4 wk), compared with 2 wk for the phosphorus smokes.

In the case of ponderosa pine, mass loading averaged 33, 55, 140 and  $206 \mu\text{g FO/cm}^2$  foliage for the four treatment/exposure durations. No symptoms were noted in the first 14 days post-treatment in the 2- and 4-hr treatments. Between 14 and 35 days, toxicity symptoms began to appear, while the intensity of damage (DMRS) did not increase, the extent



**TABLE 3.13. INFLUENCE OF FOG OIL EXPOSURE DURATION ON PHYTOTOXICITY IN PONDEROSA PINE, SHORT NEEDLE PINE, SAGEBRUSH, AND TALL FESCUE. RESULTS ARE FOR FOLIAR CONTACT TOXICITY ONLY; PLANTS WERE EXPOSED TO SGF-2 FOG OIL FOR 2, 4, 6 AND 8 HR, AT A WIND SPEED OF 2 MPH, AND RH OF 50%**

Plant Species	Exposure Duration (hr)	Time Post-Exposure (day)		
		7	14	21
Ponderosa Pine	2	0(a)	0	0
	4	0	0	0
	6	TB(0.5)1	TB(1)2	TB(2)2
	8	TB(3)1	TB(5)3	TB(6)4
Short Needle Pine	2	0	TB(0.25)1	same
	4	0	TB(1)2	TB(2)2
	6	TB(1)1	TB(2)2	TB(3)2,NS
	8	TB(3)3	TB(3)4,NS,chl	TB(4)4,NS,chl
Sagebrush	2	0	TB(0.5)2	same
	4	TB(0.25)1	TB(0.5)1	same
	6	TB(0.25)1	TB(0.25)1	same
	8	TB(0.25)2	TB(0.5)3	same
Tall Fescue	2	chl 1	TB(1.5)1, chl	TB(3)1, chl
	4	NS 2	NS 2,chl, OGA	same
	6	TB(2)5,NS,chl	TB(4)5,NS,W	TB(5)5,NS,chl,W
	8	TB(1)4,NS	TB(4)5,NS,chl,W	TB(5)5,N

(a) See Table 2.4 for definition of damage descriptors.

of damage (length of needle dieback) increased rapidly. At the higher mass loading levels (6- and 8-hr exposure), symptomology appeared earlier and progressed more rapidly in time. The amount of damage observed in the 8-hr treatment was disproportionately high based on the mass loading level, suggesting the possibility of a threshold for dose response. A similar behavior is observed for sagebrush, but is not readily apparent in tall fescue and short needle pine. As noted, mass loading values were generally higher for short needle pine than those for ponderosa pine. These averaged 104, 124, 157 and 292  $\mu\text{g FO}/\text{cm}^2$  foliage for the four treatments. The intensity and extent of damage progressed with time post-exposure and were proportional to dose. While tip burn and needle dieback were the prevalent symptoms, chlorosis and necrotic spotting of needles were apparent at the higher mass loading. The extent of foliar damage was generally less than that observed for ponderosa pine.

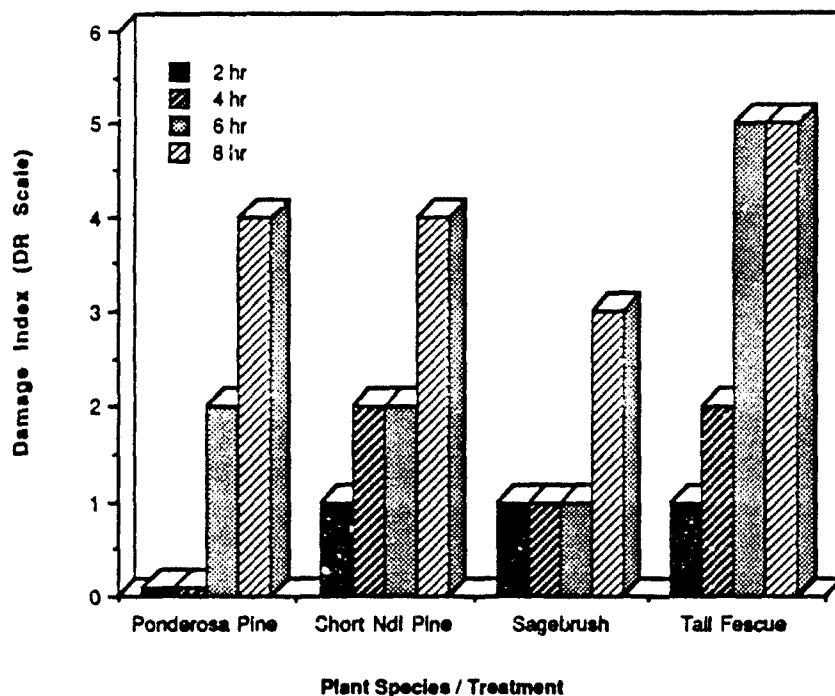


FIGURE 3.19. COMPARATIVE CONTACT TOXICITY RESPONSE OF FOUR PLANT SPECIES TO INCREASING FOG OIL DOSE

Mass loading to foliage of sagebrush averaged 82, 163, 222, and 290  $\mu\text{g FO}/\text{cm}^2$  for the 2- to 8-hr exposures. Some variability in the intensity and extent of damage was observed with sagebrush based on dose/mass loading. This is not unusual since this plant can be dead for a month before indications are apparent. The appearance of tip burn and leaf dieback was observed within 7 days of exposure, and subsequent symptomology was relatively stable for 21 days. However, at 35 days post-exposure, noticeable leaf abscission and leaf drop occurred. This was confined primarily to older leaves and should have little impact on plant survival.

Results for the grass, tall fescue, were more complex than for the other three plant species. Based on the mass loading levels, which averaged 50, 69, 129, and 238  $\mu\text{g FO}/\text{cm}^2$  foliage, the extent and intensity of effects were substantially more severe than for the other plant species studied. Early symptoms included a general chlorosis, followed by necrotic spotting of leaf blades, wilting of foliage, and subsequent onset of progressive tip burn and

dieback of blades. Effects were severe even at the lower mass loading levels; however, only the older leaves were affected. The relative severity of the effects with the grass species may be due to its relatively thin leaf cuticle and the ease of penetration by the fog oil.

While fog oil is probably not chemically toxic to plants, its presence on foliar surfaces, and subsequent penetration into the apoplast (cell walls) could have secondary effects. This would include dissolution of cell membranes, and alteration of their semi-permeability. This could account for the observed chlorosis and eventual die back of foliage.

Relative Humidity Test Series. In general, there was little difference in the plant toxicity responses observed for fog oil generated at various relative humidities. Effects were generally comparable to those reported for the fog oil range finding test. Qualitatively, the pines appear to be relatively resistant to fog oil damage, while the fescue grass and sagebrush are more sensitive. Initial results from the wind speed study, where mass loading rates are substantially elevated over those of either the range finding test or the relative humidity studies, indicated damage was much more severe. Tall fescue was heavily impacted, sagebrush was totally defoliated, while the pines were impacted least. Phytotoxicity data for the fog oil RHT series are shown in Table 3.14 and Figure 3.20.

Specific plant species responses to fog oil smokes generated at three relative humidities and with or without post exposure simulated rainfall are as follows. Ponderosa pine exhibited only minimal toxicity (intensity 1) over the first 2 wk post-exposure. At termination, there appears to be a direct relationship between RH and plant damage; however, this pattern was not observed with the other four plant species and may be simply related to the increasing ML (Table 3.8) with increased RH for the three exposures. Post-exposure leaching tends to increase the extent (the length of tip burn and dieback in cm is the value in parentheses) and intensity of damage. Since this damage is accompanied by chlorosis, the mechanism of damage would be consistent with membrane damage and leaching of essential foliar ions. Unfortunately, this premise is inconsistent with the results for the rainout treatment, where damage was minimal. In each treatment, only older growth was affected, newly formed needles exhibited little or no damage. Damage to short needle pine was generally consistent with that of ponderosa pine.

Results for sagebrush indicate only minimal damage from fog oil smokes. These appeared after the first week and remained constant over the next 2 wk. Post-exposure leaching and rainout had no effect on damage. The lack of damage probably results from the comparatively thick cuticle and cuticular structure consisting of dense mats of leaf hair, thus the lack of fog oil penetration to the cells of the leaf interior.

**TABLE 3.14. PHYTOTOXIC RESPONSES TO FOG OIL SMOKES UNDER RELATIVE HUMIDITY, RAINOUT, AND POST-EXPOSURE LEACHING CONDITIONS. PLANTS WERE EXPOSED TO SMOKES FOR 4 HR, AT 2 MPH<sup>(a)</sup>**

Plant Species	Treatment		Time Post-Exposure (days)		
	RH	Leach	7-10	14-17	24
<b>Ponderosa</b>					
Pine	20%	unleached	TB(0.5)1(b)	same	TB(1)1, OGA
		leached	TB(0.5)1	same	TB(1-2)2,chl,OGA
	64%	unleached	TB(1)1	same	TB(1-5)1,chl,OGA
		leached	TB(1)1	same	TB(1-3)2,OGA
	91%	unleached	TB(0.5-2)1	same	TB(0.5-3)3,NS,OGA
		leached	TB(0.5-2)1,chl	TB(3)2,chl	TB(2-5)3,NS,chl,OGA
Rainout		TB(0-1),OGA	same	TB(2-3)1,OGA	
<b>Short Needle</b>					
Pine	20%	unleached	TB(0.5)1	same	TB(1)1, OGA
		leached	TB(0.5)1	same	TB(1)1, OGA
	64%	unleached	TB(1-2.5)2	same	TB(3-11)3,OGA
		leached	TB(0.5-3)4	same	TB(0.5-9)5,chl,NS,OGA
	91%	unleached	0	0	TB(0-2)1,OGA
		leached	0	0	TB(0-2)1,OGA
Rainout		TB(0-1)	same	TB(0.5-4)2,chl,NS,OGA	
<b>Sagebrush</b>					
	20%	unleached	TB(0.5)1	same	TB(0.5)1, OGA
		leached	TB(0.5)1	same	TB(0.5)1, OGA
	64%	unleached	TB(0.5)1	same	TB(0.5)1, OGA
		leached	TB(0.5)1	same	TB(0.5)1, OGA
	91%	unleached	0	0	TB(0.5)1
		leached	0	0	TB(0.5)1
Rainout		TB(0.5)1, OGA	same	same	
<b>Bush Bean</b>					
	20%	unleached	NS,chl,1	same	NS,chl,2,OGA
		leached	NS,chl,1	same	NS,chl,2,OGA
	64%	unleached	LB,NS,chl,1,OGA	LB,NS,chl,3,LC	NS,chl,LB,4,LC,OGA
		leached	LB,NS,chl,1,OGA	LB,NS,chl,3,LC	NS,chl,LB,5,LC,OGA
	91%	unleached	NS,LC,2,OGA	NS,LC,2,OGA	NS,LC,chl,3,OGA
		leached	NS,1,OGA	NS,LC,chl,2,OGA	chl,NS,LC,4,OGA
Rainout		NS,chl,2,OGA	NS,chl,3,OGA	same	
<b>Tall Fescue</b>					
	20%	unleached	TB(0-2)2,chl,OGA	TB(1-6)3,chl	TB(1-8)4,OGA
		leached	TB(0-2)2,chl,OGA	TB(1-6)4,chl	TB(1-11)4,OGA
	64%	unleached	TB(0.5-2)1,chl	same	TB(0.5-7)3,chl,NS,OGA
		leached	TB(0.5-5.5)2,NS	same	TB(0.5-7)3,chl,NS,OGA
	91%	unleached	TB(0-1)2,NS,chl	TB(0.5-1)2,NS,chl	TB(1-6)3,chl,OGA
		leached	TB(0.5-1)1,NS,chl	TB(0.5-1)1,OGA	TB(0.5-4)2,chl,OGA

(a) Rainout involved 2-hr exposure to aerosol followed by 2-hr exposure to aerosol and a simulated rainfall of approximately 1 cm/hr; post-exposure simulated rainfall 0.5 cm/hr.

(b) See Table 2.4 for definition of damage descriptors.

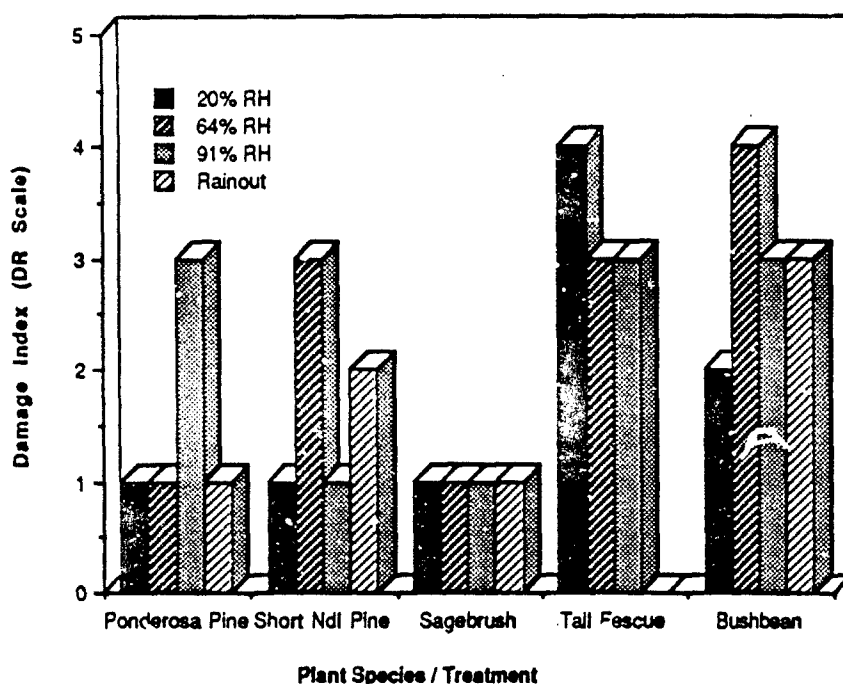


FIGURE 3.20. COMPARATIVE CONTACT TOXICITY RESPONSE OF FOUR PLANT SPECIES TO FOG OIL UNDER INCREASING MOISTURE CONDITIONS

Bush bean, as usual, exhibited a range of toxicity symptoms; although based on past data with phosphorus smokes and fog oil ML rates, damage was only moderate. Damage first appeared 4 to 7 days post-exposure, and consisted of necrotic spotting of foliage, some leaf margin burn, and chlorosis. The severity or intensity of foliar damage increased with time and affected primarily the older tissues. New trifoliates formed after exposure appeared normal; bean pods that were present during exposure developed normally, with only necrotic spotting evident. Leaching and rainout had no apparent effect on damage.

Tall fescue exhibited a surprising level of damage compared with the other native plant species. The onset of both the extent (Table 3.14, value in parentheses) and intensity of damage was rapid and included tip dieback, chlorosis, and necrotic spotting of blades. These progressed to a moderate level of damage by 24 days of post-exposure. The level of damage was comparable to that of bush bean, although the ML for the grass was approximately twice that of bush bean. Older leaf blades were primarily impacted, new leaves formed normally.

Several general comments and observations can be made based on these results. First, the overall intensity of response was low for fog oil compared with the phosphorus smokes, even though dose or ML was substantially higher. All foliar surfaces in this test were noticeably wetted with fog oil. Second, the pines and sagebrush were generally not impacted by fog oil, while the bush bean and the grass species were moderately impacted. Third, post-exposure leaching and simulated rainfall during exposure have little consistent effect on overall damage. Fourth, relative humidity appears to play no consistent role in influencing phytotoxicity. Finally, fog oil damage appears to be confined to older growth, with typical tip burn and dieback, chlorosis, and necrotic spotting of needles and leaves. First symptoms are delayed for 7 to 10 days, with only slight increases in intensity of damage over an additional two week observation period. These symptoms may result from dissolution of cell membranes by the light hydrocarbons associated with the fog oil. Therefore, it is not surprising that toxicity responses mimic phosphorus symptoms, namely osmotic damage.

Wind Speed Test Series. The toxicity of fog oil smokes, delivered at 2 to 10 mph, is shown in Table 3.15. The dose response relationships are compared based on the foliar ML rates in Table 3.12. The toxicity data clearly show the progression of effects that develop with time post-exposure and with ML or dose. Ponderosa pines exposed at various wind speeds/dose levels exhibit minimal damage at foliar ML levels of less than 600 mg/cm<sup>2</sup>; at 1400 mg/cm<sup>2</sup> only moderate damage is observed. This damage includes primarily tip burn and some chlorosis and is confined to the older needles.

Post-exposure leaching has no significant impact on damage as noted before. Sagebrush, with its higher Vd values, had the largest range in dose, 130 to 3400 µg/cm<sup>2</sup>. Fog oil effects were minimal at below 300 µg/cm<sup>2</sup>, but increased above this level. At 6 mph, 1700 mg/cm<sup>2</sup>, damage intensities increased to 3 or 4, indicating damage of 50 to 75% of the foliage. At 10 mph, and mass loadings of 3400 µg/cm<sup>2</sup>, foliar damage was severe with pronounced leaf burn and leaf drop of both the old and new leaves. Following initial leaf abscission, lateral buds initiated growth and new leaves appeared normal. Again, post-exposure leaching had no ameliorating effect on contact toxicity. Tall fescue was only moderately impacted at doses below 160 mg/cm<sup>2</sup>; while at ML of 320 and particularly 450 µg/cm<sup>2</sup>, damage was severe. Toxicity responses included relatively extensive tip burn, necrotic spotting, and chlorosis of older leaves. Younger leaves were not significantly impacted.

Changes in dry matter production for the grass are shown in Table 3.16. Fog oil exposed plants, not subjected to PEL, exhibited an average 10% reduction in dry matter

**TABLE 3.15. INFLUENCE OF WIND SPEED AND POST-EXPOSURE SIMULATED RAINFALL ON PHYTOTOXIC RESPONSES TO FOG OIL SMOKES. PLANTS WERE EXPOSED TO SMOKES FOR 1 HR AT 60% RH.**

Plant Species	Treatment (WS, mph)	Leach	Time Post-Exposure (days)		
			7	16	24
Ponderosa Pine	2	unleached	0(a)	0	0
		leached	0	0	0
	4	unleached	0	TB(0.5-2)1	same
		leached	0	TB(0.5-2)1	same
	6	unleached	0	TB(0.5-2)1	same
		leached	0	TB(0.5-2)1	same
	10	unleached	TB(0.5-1)1	TB(1-5)2	TB(1-5)2,OGA
		leached	TB(0.5-1)2,chl	TB(1-2)2,chl	TB(1-2)2,chl,OGA
Sagebrush	2	unleached	0	0	0
		leached	0	0	0
	4	unleached	0	TB(0.5)1	same
		leached	0	TB(0.5)1	same
	6	unleached	0	TB(0.5)2,OGA	TB(1)3,O&NGA
		leached	0	TB(1)3,O&NGA	TB(1)4,O&NGA
	10	unleached	LBD,3,O&NGA	LBD,5,O&NGA	same(b)
		leached	LBD,3,O&NGA	LBD,5,O&NGA	same(b)
Tall Fescue	2	unleached	0	TB(0.5)2, chl	same
		leached	0	TB(0.5)2,chl	same
	4	unleached	0	TB(0.5)2,NS,chl,OGA	same
		leached	0	TB(0.5)2,NS,chl,OGA	same
	6	unleached	0	TB(0.5-5)3,NS,chl,OGA	TB(1-6)4,NS,chl,OGA
		leached	0	TB(0.5-5)3,NS,chl,OGA	TB(1-5)3,NS,chl,OGA
	10	unleached	chl,2,OGA	TB(0.5-6)3,NS,chl,OGA	same
		leached	chl,2,OGA	TB(0.5-6)5,NS,chl,OGA	same

(a) See Table 2.4 for definition of damage descriptors.

(b) Severely impacted sagebrush plants exhibited lateral bud growth at the point approximately 50 to 70% defoliation. New growth appeared normal.

production (n.s.,  $P \geq 0.05$ ) over the 27-day post-exposure period, at the three lowest wind speeds. At the higher wind speed there was a 30% reduction in dry weight. Post-exposure leaching had no significant effect on dry matter production at doses below  $300 \mu\text{g}/\text{cm}^2$ , but appeared to have a negative effect at doses of  $450 \mu\text{g}/\text{cm}^2$  ( $P \leq 0.01$ ).

Overall, the toxicity of fog oil smoke, on a dose (ML) basis, is substantially less than that observed for red or white phosphorus smokes. It would appear that the fog oil toxicity results from penetration of the light hydrocarbons into the leaves and subsequent dissolution of cell membrane components. This is based on the visual wetting of leaves by deposited fog oil,

**TABLE 3.16. EFFECT OF SGF-2 FOG OIL AND POST-EXPOSURE SIMULATED RAINFALL ON DRY MATTER PRODUCTION IN TALL FESCUE EXPOSED AT DIFFERENT WIND SPEEDS (1 HR EXPOSURE, 60% RH)**

Exposure Code	Condition (WS, mph)	Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ foliage)	Dry Matter Production (gm dry wt)(a)	
			w/o PEL	w/PEL(b)
FO-17	2	70 $\pm$ 23	5.66 $\pm$ 0.32 +	5.20 $\pm$ 0.57 +
FO-19	4	163 $\pm$ 50	6.28 $\pm$ 0.29 -	6.46 $\pm$ 0.86 -
FO-20	6	321 $\pm$ 145	5.60 $\pm$ 0.69 -	5.17 $\pm$ 0.93 -
FO-18	10	450 $\pm$ 153	4.84 $\pm$ 0.07 +++	4.32 $\pm$ 0.08 +++
	Control	0	6.50 $\pm$ 0.27	

(a) Avg  $\pm$  s.d., n=3; Student t-test,  $P \leq 0.01$ (+++),  $P \leq 0.05$ (++),  $P \leq 0.1$ (+), not significant from control (-).

(b) Post-exposure simulated rainfall (PEL) simulated a 0.5 cm/hr rainfall. Data for first harvest, 27 days post-exposure.

the prevalence of chlorosis, and the localized necrosis observed on exposed foliage. This type of damage, which is common with oil-based herbicides, would result in osmotic problems as evidenced by the symptomology. The lack of impact reduction by rainout and post-exposure leaching indicates that the fog oil readily dissolves into the foliar waxes and cuticular structures. Initial results (not presented) indicate that fog oil deposited to foliage and soil surfaces is rapidly lost. Studies are currently underway to evaluate the half-life of fog oil in these systems. Preliminary data suggest that observed losses may be due to the rapid volatilization of light hydrocarbons.

**Cumulative Dose Test Series.** The purpose of the CDT, involving nine consecutive exposures over a 3-wk period, is to determine if total ML of smoke constituents to foliar surfaces is additive with respect to phytotoxicity, or if plant compensation to the chemical insult can reduce the end response. Plants were exposed to either low or high FO concentrations; exposures were for 4 hr, 3 times per week for 3 wk. Foliar contact toxicity data are presented in Table 3.17.

In the low dose treatment, ML to foliar surfaces following the nine-exposure sequence ranged from 17 to 32  $\mu\text{g FO}/\text{cm}^2$  foliage; foliar ML in the high dose treatment ranged from 242 to 754  $\mu\text{g FO}/\text{cm}^2$ . It should be noted that these values are significantly lower than the actual ML, due to the rapid loss of volatile components of FO from foliar surfaces; see section on "Environmental Persistence" that follows. Results for the low dose treatment indicate that adverse effects from FO smokes at low doses are non-existent or minimal for tall fescue, ponderosa pine, and sagebrush. Minimal effects occur 3 wk after the final exposure.



ponderosa pine, and sagebrush. Minimal effects occur 3 wk after the final exposure.

**TABLE 3.17. IMPACT OF CUMULATIVE DOSING WITH SGF-2 FOG OIL ON PHYTOTOXIC RESPONSES IN PONDEROSA PINE, SAGEBRUSH, BUSH BEAN, AND TALL FESCUE. PLANTS EXPOSED TO LOW OR HIGH AIR CONCENTRATIONS NINE CONSECUTIVE TIMES FOR 4 HR EACH OVER A 3-WK PERIOD.**

Dose Level <sup>1</sup>	Plant Species	Post-Exposure Effects <sup>(a)</sup> (wk)		
		1	2	3
Low	Ponderosa Pine	0(b)	0	1, TB
	Sagebrush	0	0	1, chl
	Bush Bean	2, NS	3, chl	3, chl, NS, OGA
	Tall Fescue	0	0	0
High	Ponderosa Pine	1, TB, chl, OGA	1, same	4, TB, NS, O&NGA
	Sagebrush	4, TB, Wt, LD, O&NGA	5, same	5, TB, OGA
	Bush Bean	5, LB, NS, chl, LD, OGA	4, LD, NG healthy	3, chl, TB, LB, OGA
	Tall Fescue	4, NS, chl, TB, OGA	3, same, NG healthy	3, same

(a) Foliar mass loading rates for ponderosa pine, sagebrush, bush bean and tall fescue were  $32 \pm 7$ ,  $52 \pm 3$ ,  $17 \pm 3$  and  $29 \pm 5$   $\mu\text{gFO}/\text{cm}^2$  for the low dose treatment, and  $242 \pm 33$ ,  $754 \pm 328$ ,  $213 \pm 25$  and  $421 \pm 34$   $\mu\text{gFO}/\text{cm}^2$ , respectively, for the high dose treatment.

(b) See Table 2.4 for definition of damage descriptors.

In the high dose treatment, adverse effects were much more pronounced for all plant species. Ponderosa pine exhibited a delayed response, involving chlorosis, tip burn, and necrotic spotting of the needles. While only the older growth was impacted at one and two wk, new growth exhibited effects by the third week post-exposure. Sagebrush showed a rapid and severe onset of toxicity. This included tip burn, wilting, and leaf drop, and affected both young and old tissues. By 3 wk, plants were partially defoliated, with new growth exhibiting only tip burn. The damage to bushbean was severe, with a DR value of 5. This involved leaf burn, necrotic spotting, chlorosis, and leaf drop of older leaves by one week post-exposure. Over the subsequent 2 wk, the overall damage rating was reduced by the normal growth of new tissues. In tall fescue, initial damage to older leaves was severe, with general necrotic spotting, chlorosis and tip burn of the canopy. However, overall toxicity was reduced in subsequent weeks by the normal growth of new foliage.

It would appear from the contact toxicity data and their corresponding mass loading data that we are not seeing a compensation by the plants in response to FO contamination. This is more so for the broad leaf and pine species than the grass. On a dose basis, effects are at least as severe as those observed for the RFT, RHT, and WST at comparable foliar mass loadings. This is contrary to the reported observations for the phosphorus smokes.

The rapid loss of fog oil from foliage, most likely caused by volatilization, explains the relatively high variability in mass loading values for replicate treatments and the unexpectedly low ML recorded at the end of the cumulative dose test. Based on the depuration data and calculated half-time for fog oil, it is estimated that the actual mass loading in the absence of these losses would be a factor of 5 to 10 higher. This difference explains the higher degree of phytotoxic response seen in the CDT compared with either the RHT or the WST series at comparable mass loadings. It should be noted that foliar persistence, as described here, would be increased under cooler temperature regimes, and reduced further at higher temperatures and higher light intensities than provided under present growth chamber conditions.

### 3.6 RESIDUAL EFFECTS OF FOG OIL ON PLANT GROWTH

The purpose of the residual effects studies was to determine whether foliar contaminants are absorbed by perennial plants, transported to the roots, and then have a residual influence on plant viability and performance. These studies were conducted with tall fescue, since it is the only rapidly growing perennial employed in these studies, and evaluate changes in biomass production following foliar contamination and cropping. At 35 days post-exposure, the tall fescue grass from the foliar contact toxicity studies were harvested, and plants allowed to regrow for two successive 45-day harvests.

Relative Humidity Test Series. In this test series, plants were exposed to FO smokes at windspeeds of 2 mph, at a range of RH and rainout conditions. A subset of plants exposed at each RH were subjected to a post-exposure simulated rainfall (PEL) to evaluate the ameliorating effect, if any, of contaminant wash-off events. The results shown in Tables 3.18 and 3.19 provide the biomass production data for tall fescue at 25-days post-exposure, and 30-days following cutback and harvest, and show the effect of PEL on biomass production.

At the first harvest, there is a significant overall reduction (35%) in biomass production for all treatments when compared to controls (Table 3.18). This reduction is most likely due to the dieback of the older leaves of these plants following exposure, with the only dry matter contribution for treated plants coming from new growth. In the second harvest, residual effects of foliarly absorbed, and root retained, FO contaminants are clearly evident. At the low RH exposures, there is a 60% reduction in dry matter production; this adverse effect is dramatically reduced, but still significantly lower than controls, at the higher RH (91%) and in the rainout treatments. The PEL treatment had no significant ameliorating effect on the response (Table 3.19). While it is clear that the higher RH and rainout conditions result in less adverse impact, the reasons are unclear. It is probable that, under high atmospheric moisture levels, the

**TABLE 3.18. EFFECT OF SGF-2 FOG OIL AND POST-EXPOSURE SIMULATED RAINFALL ON DRY MATTER PRODUCTION IN TALL FESCUE EXPOSED AT DIFFERENT RELATIVE HUMIDITIES AND UNDER RAINOUT CONDITIONS. PLANTS EXPOSED FOR 4 HR AT 2 MPH(a)**

Exposure Code	Condition (% RH)	Foliar Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ )	Dry Matter Production (g dry wt)(b)	
			First Harvest	Second Harvest
FO-12	20 w/PEL	239 $\pm$ 70	3.59 $\pm$ 0.47 +++	2.81 $\pm$ 0.16 +++
			3.40 $\pm$ 0.06 +++	2.60 $\pm$ 0.13 +++
FO-14	64 w/PEL	401 $\pm$ 109	3.22 $\pm$ 0.11 +++	2.65 $\pm$ 0.26 +++
			3.21 $\pm$ 0.64 +++	2.96 $\pm$ 0.17 +++
FO-15	91 w/PEL	320 $\pm$ 69	4.00 $\pm$ 0.24 +++	5.36 $\pm$ 0.28 +++
			3.97 $\pm$ 0.09 +++	4.88 $\pm$ 0.28 +++
FO-16	Rainout	377 $\pm$ 173	3.79 $\pm$ 0.26 +++	5.09 $\pm$ 0.23 +++
	Control	0	5.31 $\pm$ 0.10	6.64 $\pm$ 0.31

(a) Rainout involved 2-hr exposure to aerosol, followed by 2-hr exposure to aerosol in the presence of a simulated rainfall of approximately 1 cm/hr. Post-exposure simulated rainfall (PEL) simulated a 0.5-cm/hr rainfall. Data for first harvest, 25 days post-exposure, and second harvest represent 30 days of regrowth.

(b) Avg $\pm$ s.d., n=4; Student t-test,  $P \leq 0.01$ (+++).

cuticular surfaces of plants may become hydrated to an extent that precludes or limits the penetration of the FO contaminants into the lipid/wax components of plant surfaces.

**Wind Speed test series.** In the WST series, the grasses were exposed to a wider range of FC mass loading levels, thereby providing some indication of dose response. Results are provided in Table 3.20. Foliar mass loading levels ranged from 70 to 450  $\mu\text{g FO}/\text{cm}^2$  and therefore, at the high end, overlapped the doses from the RH tests. The first harvest results indicate little effect on dry-matter production at foliar loading rates below 300  $\mu\text{g FO}/\text{cm}^2$ . No explanation of the inhibitory response of the 2-mph treatment is evident. At 10 mph, where loading rates were at 450  $\mu\text{g}/\text{cm}^2$ , there was a 25% reduction in biomass production. Application of a PEL regime had no significant effect on dry matter production, except at the higher 10-mph doses. As observed for the RH test, the second harvest data show a residual impact of the prior foliar contamination event. In fact, there is a clear inverse relationship between foliar mass loading and biomass production. This is observed even at the lower 4-mph dosing level.

**TABLE 3.19.** INFLUENCE OF POST-EXPOSURE LEACHING ON DRY MATTER PRODUCTION IN TALL FESCUE EXPOSED AT DIFFERENT RELATIVE HUMIDITIES, AND UNDER RAINOUT CONDITIONS. PLANTS EXPOSED FOR 4 HR, AT 2 MPH(a).

Exposure Code	Relative Humidity (%)	Mass Loading ( $\mu\text{g FO/cm}^2$ foliage)	Dry Matter Production (gm dry wt)(b)	
			w/o PEL	w/PEL
FO-12	20	239 $\pm$ 70	3.59 $\pm$ 0.47 +++	3.40 $\pm$ 0.06 +++
FO-14	64	401 $\pm$ 109	3.22 $\pm$ 0.11 +++	3.21 $\pm$ 0.64 +++
FO-15	91	320 $\pm$ 69	4.00 $\pm$ 0.24 +++	3.97 $\pm$ 0.09 +++
FO-16	Rainout	377 $\pm$ 173	3.79 $\pm$ 0.26 +++	ND
	Control	0	5.31 $\pm$ 0.10	

(a) Rainout involved 2-hr exposure to aerosol followed by 2-hr exposure to aerosol in the presence of a simulated rainfall of approximately 1 cm/hr; post-exposure simulated rainfall (PEL) simulated a 0.5-cm/hr rainfall; ND, not determined. Data for first harvest, 25 days post-exposure.

(b) Avg $\pm$ s.d., n=3; Student t-test,  $P \leq 0.01$ (+++).

**TABLE 3.20.** EFFECT OF SGF-2 FOG OIL AND POST-EXPOSURE SIMULATED RAINFALL ON DRY MATTER PRODUCTION IN TALL FESCUE EXPOSED AT DIFFERENT WIND SPEEDS. PLANTS EXPOSED FOR 1 HR, AT 60% RHT(a).

Exposure Code	Condition (WS, mph)	Foliar Mass Loading ( $\mu\text{g FO/cm}^2$ )	Dry Matter Production (g dry wt)(b)	
			First Harvest	Second Harvest
FO-17	2 w/PEL	70 $\pm$ 23	5.66 $\pm$ 0.32 +++	6.08 $\pm$ 0.25 -
			5.20 $\pm$ 0.57 +++	6.32 $\pm$ 0.18 -
FO-19	4 w/PEL	163 $\pm$ 50	6.28 $\pm$ 0.29 -	5.41 $\pm$ 0.58 ++
			6.46 $\pm$ 0.66 -	5.40 $\pm$ 0.18 ++
FO-20	6 w/PEL	321 $\pm$ 145	5.60 $\pm$ 0.69 ++	4.44 $\pm$ 0.94 ++
			5.17 $\pm$ 0.93 +++	5.15 $\pm$ 0.43 +++
FO-18	10 w/PEL	450 $\pm$ 153	4.84 $\pm$ 0.07 +++	3.44 $\pm$ 1.10 ++
			4.32 $\pm$ 0.08 +++	2.89 $\pm$ 0.76 +++
	Control	0	6.50 $\pm$ 0.27	6.30 $\pm$ 0.32

(a) Post-exposure simulated rainfall (PEL) simulated a 0.5-cm/hr rainfall. Data for first harvest, 27 days post-exposure, and second harvest represent 30 days of regrowth.

(b) Avg $\pm$ s.d., n=4; Student t-test,  $P \leq 0.01$ (+++),  $P \leq 0.05$ (++), not significant from control (-).

Cumulative Dose Test Series. Mass loading levels for the CDT series were 29 and 421  $\mu\text{g FO/cm}^2$  foliage for the low and high dose treatments, respectively. As noted above for this test, ML levels are low due to volatile losses. Actual mass loading levels should have been approximately 300 and 1200  $\mu\text{g/cm}^2$ . First harvest results (Table 3.21) indicate no adverse effect at the low dose regime. However, at the high dose regime there is an approximately 60% reduction in dry matter production. The second harvest at the high dose regime shows a 30% growth reduction, and again indicates the presence of a residual effect. A comparison of the CDT second harvest growth reduction (30%) with that obtained in the RHT (approximately 60%) under similar conditions (Table 3.18, second harvest for 20 and 64% RH treatments), indicates that the overall residual impact of foliar exposure to FO smokes is less following cumulative dosing compared with a single event of the same or lower dose. This would indicate that some plant compensation or amelioration of toxic components does occur in tall fescue with respect to residual effects on subsequent plant growth. This amelioration of effects may result from the loss and/or metabolism of tissue absorbed fog oil between dosing events. This amelioration was not noted in the CDT contact data presented in Table 3.17, which basically spans the period from first exposure through the first harvest.

### 3.7 INDIRECT EFFECTS OF FOG OIL ON PLANT GROWTH

Plant effects resulting from direct contact toxicity of smokes with foliar surfaces in many instances can be short-term and transient in nature. In some instances, as seen in the residual growth effects in tall fescue, adverse effects such as growth reductions are persistent even in the absence of visual symptomology. The purpose of the indirect effects studies is to determine whether soils, when contaminated with an obscurant smoke, can be altered sufficiently to impact subsequent plant growth. In these studies, indirect effects were evaluated with the same perennial grass, tall fescue. Soils exposed to the smoke and subsequently planted with the grass. Treatments were monitored for percent germination, blade length, dry matter production, and visual symptomology. Plants were carried through at least two harvests to permit evaluation of the amelioration of any impacts resulting from soil contamination. Two soil types were employed, which included a Burbank sandy loam characteristic of the semi-arid regions of central Washington state and a Maxey Flats silty-clay from Kentucky.

Range Finding Test Series. Pots containing Burbank and Maxey Flats soils were exposed to fog oil smokes for 2, 4, 6, and 8 hr. These were subsequently seeded with tall fescue to evaluate any adverse effects of fog oil on both seed germination and vegetative plant growth. Mass loadings to soil surfaces were similar for the two soils and averaged 90, 160, 240, and 330  $\mu\text{g FO/cm}^2$  soil surface for the four treatments. Following germination, plants

**TABLE 3.21. INFLUENCE OF FOG OIL FOLIAR CONTAMINANTS ON GROWTH AND REGROWTH OF TALL FESCUE FOLLOWING CUMULATIVE DOSING. INVOLVES NINE CONSECUTIVE EXPOSURES OF 4 HR DURATION OVER A 3-WEEK PERIOD; WIND SPEED 2 MPH, 20% RH**

Exposure Code	Dose Level	Foliar Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ )	Dry Matter Production(a)	
			First Harvest (g dry wt)(b)	Second Harvest
FO-22	Low	$29 \pm 5$	$5.39 \pm 0.35 -$	$3.32 \pm 0.37 -$
	High	$421 \pm 34$	$2.62 \pm 0.39 +++$	$2.32 \pm 0.33 ++$
	Control	0	$5.86 \pm 0.42$	$3.20 \pm 0.43$

(a) Data for first harvest, 21 days post-exposure, and second harvest represents 32 days of regrowth.

(b) Avg $\pm$ s.d., n=4; Student t-test,  $P \leq 0.01(+++)$ ,  $P \leq 0.05(++)$ , not significant from control (-).

were allowed to grow for 100 days, and any effects on dry matter production noted. Results of the first harvest are shown in Table 3.22.

As with the phosphorus smokes (Van Voris et al. 1987), no adverse effect was noted on percent germination for the grass species grown on either of the fog oil contaminated soils. Overall growth of the grass species, on a biomass basis, was better on the more fertile Burbank sandy loam than the Maxey Flat silty-clay soil. Within each soil treatment, there was no significant effect on dry matter production over the untreated control soils. These results would suggest little adverse impact of moderate soil loadings of fog oil on seed germination and plant growth. Results from the wind speed and cumulative dose tests, with their higher mass loadings, should provide a better basis for assessment of indirect fog oil effects.

Relative Humidity Test Series. In the RHT series, soils were exposed to fog oil smokes delivered under a range of RH conditions, in addition to simulated rainout conditions. Results are shown in Table 3.23. No effect of fog oil on germination was noted for either soil; this is consistent with our previous findings. First harvest results for grasses grown on Burbank soil, indicate a significant growth reduction for soils exposed only at 20% RH and under rainout conditions; at 20% RH, a moderate degree of tip burn occurred compared to the controls and higher RH treatments. Following harvest and regrowth, second harvest results show that the growth reduction at 20% RH is reduced but persistent; this reduction amounted to 30% of controls compared to 60% of controls for the first harvest. Growth reductions are also significant for the 64% and 91% RH treatments, indicating a lasting residual effect of fog oil in soils.

**TABLE 3.22. INDIRECT EFFECTS OF SGF-2 FOG OIL SMOKE DEPOSITED TO SOIL ON GROWTH OF TALL FESCUE. GROWTH DURATION WAS 100 DAYS POST-EXPOSURE**

Soil Type	Exposure Duration (hr)	Dry Matter Production (gm)(a)
Burbank Sandy Loam	Control	3.27 ± 1.81
	2	3.03 ± 0.41 -
	4	3.17 ± 0.07 -
	6	2.89 ± 0.01 -
	8	3.20 ± 0.24 -
Maxey Flats Silty-Clay	Control	1.10 ± 0.07
	2	1.01 ± 0.11 -
	4	1.14 ± 0.18 -
	6	1.16 ± 0.12 -
	8	1.03 ± 0.20 -

(a) Avg ± s.d., n=4; Student t-test, not significant from control (-).

First harvest results for Maxey Flats soil indicate a more pronounced overall effect. Growth reductions were significant for the 20%, 64%, and 91% RH treatments, and for the rainout treatment. Blade tip burn was evident in each of the three RH treatments. Growth reductions were somewhat less in the second harvest, as were visual symptoms. Growth reductions were still highest at the lower RH treatment.

Preliminary evaluation of the effects of fog oil on soil nutrient levels were negative, as would be expected. Results from the indirect soil effects studies, regrowth studies following foliar contamination, and the contact toxicity studies indicate that fog oil damage is more severe and more persistent when exposure is conducted at low relative humidity. One could postulate that higher moisture levels wet the sorptive surfaces of foliage and soils, thereby limiting the penetration of the hydrocarbons into their molecular structures. While this is plausible for the problem of contact toxicity, it does not explain the soil results.

Wind Speed Test Series. In the WST series, soils were exposed to fog oil smokes at 2, 4, 6, and 10 mph, at 20% RH. Since the low RH treatments exhibited a maximum effect, the wind speed test provides a convenient data set for the evaluation of the relationship between mass loading and soil/plant effects (Table 3.24). With Burbank soil, no significant effects on dry-matter production are apparent for wind speeds below 6 mph or mass loading levels of 225 µg FO/cm<sup>2</sup> soil. At 10 mph (475 µg FO/cm<sup>2</sup>), there is a 25% growth reduction. In the second

**TABLE 3.23. INDIRECT EFFECTS OF FOG OIL SMOKES DEPOSITED TO SOILS UNDER VARIOUS MOISTURE REGIMES ON THE GROWTH OF TALL FESCUE**

Soil Type	Treatment Condition(a) (RH% at 2 mph)	First Harvest (100 days)			Second Harvest (60 days)		
		Height (cm)	Yield(b) (g dry wt)	Toxicity (DR Rating)	Height (cm)	Yield(b) (g dry wt)	Toxicity (DR Rating)
Burbank Sandy Loam	20	27	0.77 ± 0.30 ++	2	33	3.79 ± 0.66 ++	1
	64	36	1.97 ± 0.34 -	1	34	4.49 ± 0.48 ++	1
	91	32	1.60 ± 0.49 -	1	32	4.60 ± 0.10 ++	0
	Rainout	33	1.52 ± 0.03 +	0	34	5.01 ± 0.34 -	0
	Control	34	1.86 ± 0.28	0	33	5.53 ± 0.17	0
Maxey Flats Silty-Clay	20	30	0.89 ± 0.70 +++	3	33	2.42 ± 1.73 ++	1
	64	36	1.89 ± 0.49 +	2	33	3.67 ± 0.66 +	1
	91	35	1.88 ± 0.28 ++	2	35	4.37 ± 0.70 -	0
	Rainout	35	1.77 ± 0.32 ++	2	34	3.69 ± 0.12 +	0
	Control	39	2.56 ± 0.31	0	34	4.61 ± 0.26	0

(a) Soil mass loading rates for the 20, 64, 91% and rainout treatments were 697 ± 11, 976 ± 66, 777 ± 40 and 829 ± 110 µg FO/cm<sup>2</sup> for Burbank soil, and 639 ± 137, 783 ± 68, 702 ± 4, and 790 ± 58 µg FO/cm<sup>2</sup> for the Maxey Flats soil.

(b) Avgts.d., n=4; Student t-test, P≤0.01(+++), P≤0.05(++), P≤0.1(+), not significant from control (-).

**TABLE 3.24. INDIRECT EFFECTS OF FOG OIL SMOKES DEPOSITED TO SOILS AT VARIOUS WIND SPEEDS, ON GROWTH OF TALL FESCUE. RELATIVE HUMIDITY MAINTAINED AT 20% FOR ALL TESTS, EXPOSURE DURATION 1 HR**

Soil Type	Treatment Condition(a) (mph at 20% RH)	First Harvest (60 days)			Second Harvest (60 days)		
		Height (cm)	Yield(b) (g dry wt)	Toxicity (DR Rating)	Height (cm)	Yield(b) (g dry wt)	Toxicity (DR Rating)
Burbank Sandy Loam	2	33	1.30 ± 0.21 -	2	30	4.98 ± 0.33 +++	1
	4	33	1.60 ± 0.30 -	2	31	6.08 ± 0.36 -	1
	6	33	1.63 ± 0.11 -	1	31	5.93 ± 0.24 -	0
	10	31	1.21 ± 0.16 +++	2	30	5.22 ± 0.75 +	0
	Control	34	1.60 ± 0.18	0	33	6.32 ± 0.24	0
Maxey Flats Silty-Clay	2	36	1.66 ± 0.13 +	0	34	5.56 ± 0.48 -	1
	4	35	1.54 ± 0.35 +	1	32	3.94 ± 2.26 -	0
	6	31	0.96 ± 0.21 +++	2	32	2.28 ± 1.41 -	0
	10	32	0.90 ± 0.33 +++	3	37	4.54 ± 1.86 -	0
	Control	34	1.92 ± 0.24	0	36	4.06 ± 2.28	0

(a) Soil mass loading rates for the 2-, 4-, 6- and 10-mph treatments were 158 ± 18, 178 ± 66, 225 ± 30 and 475 ± 121 µg FO/cm<sup>2</sup> for Burbank soil, and 109 ± 37, 170 ± 53, 209 ± 44, and 298 ± 69 µg FO/cm<sup>2</sup> for the Maxey Flats soil.



(b) Avg $\pm$ s.d., n=4; Student t-test,  $P\leq 0.01$ (+++),  $P\leq 0.1$ (+), not significant from control (-).

harvest, the effects of the higher soil doses on growth are ameliorated. The significance of the low dose treatment results cannot be readily explained. In the Maxey Flats soil, there is a more pronounced correlation of soil dose/wind speed with reductions in growth. This ranges from a 14% reduction in growth for the 2-mph treatment, to a 50% reduction at 10 mph. The second harvest results show no significant differences between treatments and controls, although there is substantial variability in this particular data set.

Cumulative Dose Test Series. The results for the CDT series are provided in Table 3.25 for the three harvests of Tall Fescue grown on soils contaminated in the cumulative dose test series. The purposes of this test are to assess the cumulative impact of recurrent smoke use on soils and the performance of plants grown on these soils. This test series normally provides the highest mass loading levels evaluated. As with the other fog oil test series, no effect on germination was noted. From the dry matter production data shown in Table 3.25, it is clear that there is no significant effect of fog oil on plants grown in contaminated Burbank soil. First harvest results for Maxey Flats soil, however, indicate a significant growth reduction ( $P\leq 0.1$ ), particularly in the high dose treatment. This growth inhibition is not sustained in the subsequent two harvests, and treatment values are similar to controls. It is assumed that the amelioration of effects in the Maxey Flats soil results from either volatilization of the fog oil from soil, or its decomposition. In either case the dose is reduced and impacts eliminated. The observed differences in plant response when grown on these two soils may be related to the lower overall volatility of residual oil in the Maxey Flats compared with Burbank soil.

### 3.8 SOIL MICROBIAL EFFECTS

The effect of fog oil smoke on soil microbial populations and soil microbially mediated processes was evaluated. The soil microbial population plays a key role in nutrient cycling and the biodegradation of organic compounds in soil. The decomposition of organic material in soil into mineral forms and the cycling of plant nutrients are mediated by the soil microbial processes.

The decomposition of organic matter by the soil microbial population is critical to the cycling of important nutritional elements (nitrogen, phosphorus, sulfur, and some trace metals). Soil microbial decomposition processes also detoxify xenobiotic chemicals that may be released to the environment. Therefore, any physical or chemical perturbation on the soil system that disrupts these microbially mediated processes can indirectly influence plant growth and directly affect the soil's ability to decompose organic matter and detoxify xenobiotics.

**TABLE 3.25. INDIRECT EFFECTS OF FOG OIL CONTAMINATION OF SOILS, FOLLOWING CUMULATIVE DOSING, ON GROWTH OF TALL FESCUE(a)**

Harvest	Growth Duration (wk)	Dry matter Production (g dry weight)(b)	
		Burbank	Maxey Flats
First Harvest	6		
Control		7.52 ± 0.24	5.22 ± 0.30
Low		7.38 ± 0.36 -	4.19 ± 0.50 +
High		7.80 ± 0.51 -	3.68 ± 1.06 +
Second Harvest	8		
Control		13.95 ± 0.88	11.86 ± 0.63
Low		14.48 ± 0.26 -	11.55 ± 0.42 -
High		14.10 ± 0.39 -	10.47 ± 1.45 -
Third Harvest	4		
Control		3.09 ± 0.27	2.57 ± 0.23
Low		3.02 ± 0.25 -	2.51 ± 0.09 -
High		2.87 ± 0.11 -	2.41 ± 0.36 -

(a) Soil mass loading levels were 250 and 1125 µg FO/cm<sup>2</sup>, for the low and high dose treatments, respectively; not corrected for losses due to volatilization.

(b) Avg±s.d., n=4; Student t-test, P≤0.1(+), not significant from control (-).

Soil enzyme activity and respiration are indicative of the activity of the cumulative heterotrophic microbial population. Soil respiration is one of the most frequently used indexes of microbial activity in soil (Anderson 1982). Soil dehydrogenase activity has been used in the past to measure the activity of the soil microbial population and is an index of endogenous soil microbial activity (Moore and Russell 1972). Dehydrogenase enzymes are intracellular and involved in microbial respiratory processes necessary for the breakdown of organic compounds in soil.

Nitrogen is the nutrient most limiting in agricultural (Stevenson 1982) and arid land ecosystems (West and Skujins 1978). Nitrogen is considered a macronutrient because plants require large quantities of this element for growth. Nitrogen is also an essential element for the soil microbial population. The conversion of organic nitrogen to available inorganic forms combines two distinct microbiological processes: ammonification, which converts organic nitrogen to ammonia; and nitrification, which transforms ammonia to nitrate. Nitrification in soil is mediated by nitrifying bacteria, or nitrifiers. The *Nitrosomonas* spp. are most responsible for the conversion of ammonia to nitrite and the *Nitrobacter* spp. for the further oxidization of nitrite

to nitrate, a soluble and mobile form in soil used by plants and other microorganisms.

Soil organisms are also sources of food for the soil fauna (e.g., mites, arthropods, worms) and thus occupy an important position low in the food chain. A deleterious impact on the various soil microbial populations can affect soil invertebrate life and the soil-dwelling animals that depend on these populations for food.

The effects of fog oil smokes on the soil microbial community, therefore, were evaluated with these three principal soil microbiological parameters, namely, soil respiration, soil dehydrogenase enzyme activity, and soil nitrifying bacteria populations.

Soil Respiration. Soil respiration is indicative of the activity of the cumulative heterotrophic microbial population. It can be measured by CO<sub>2</sub> evolution or O<sub>2</sub> consumption, or both. Heterotrophic activity is responsible for the decomposition of natural and xenobiotic carbon compounds in soils as well as for the cycling and mineralization of essential inorganic nutrients such as nitrogen, phosphorus and sulfur.

Respiration of Palouse soil was not inhibited by the fog oil smoke exposures in all the tests conducted, as shown in Figures 3.21 (20% and 91% RH), 3.22 (10 mph), and 3.23 (cumulative dose). Standard deviations associated with several of the treatments shown on these figures were low and graphically unresolved. In Figure 3.21, the average and standard deviations for the control + glucose, control and exposed soils at 257 hr were  $113 \pm 0.2$ ,  $24.2 \pm 2.2$ , and  $28.1 \pm 0.2$  for the 20% RH treatment, respectively. For the 91% RH treatment, values were  $110 \pm 0.1$ ,  $38.6 \pm 1.5$ , and  $38.6 \pm 0.1$ , respectively. In the wind speed test, Figure 3.22, oxygen consumption values at 74 hr were  $52.3 \pm 1.2$ ,  $12.2 \pm 0$  and  $13.0 \pm 0.3$ , respectively. In the cumulative dose test, average  $\pm$  standard deviation values for the control and exposed soils were 33.8 (second replicate data lost) and  $38.7 \pm 0.9$ , respectively.

These results indicate that fog oil probably is not a toxicant to the soil heterotrophic microbial activity. An unexposed control soil amended with 150 mg glucose was included in each assay to ensure that a viable heterotrophic population was indeed present as evidenced by the substantial increase in oxygen consumption. Further, since much of the hydrocarbons of fog oil may not be readily utilized as substrate by the unadapted soil biomass, a small component of the oil may be readily metabolized. Alternatively, a subpopulation of the soil microbial biomass may be able to utilize the complex hydrocarbons in the oil, accounting for the slight increase in soil respiration that was observed.

Soil Dehydrogenase Activity. The inhibition of enzymes that drive key metabolic reactions in microbial cells is likely the underlying cause of chemical toxicity. Microbial

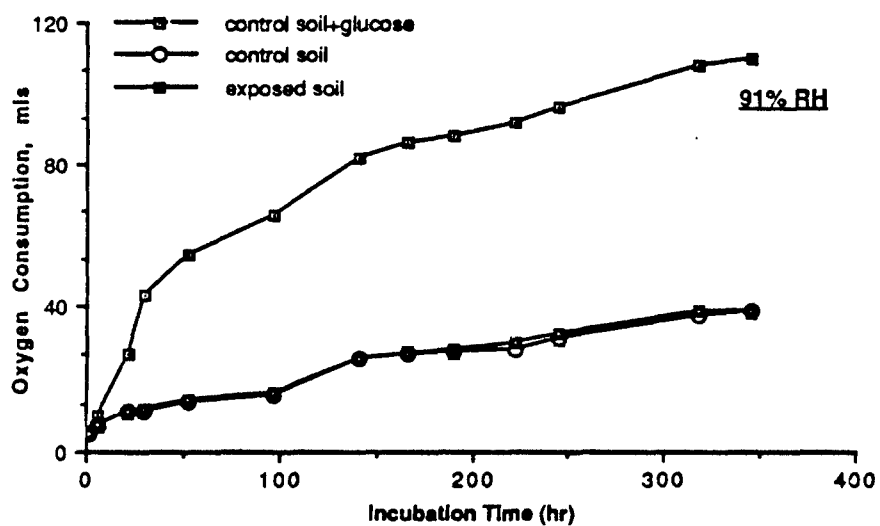
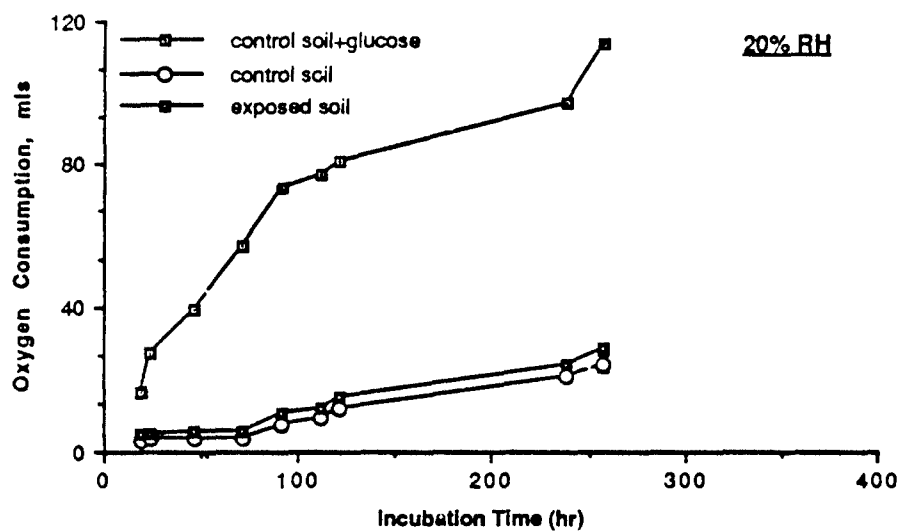


FIGURE 3.21. EFFECTS OF FOG OIL EXPOSURES (20% AND 91% RH) ON PALOUSE SOIL RESPIRATION. ERROR BARS (see text) REPRESENT STANDARD DEVIATIONS, N=2.

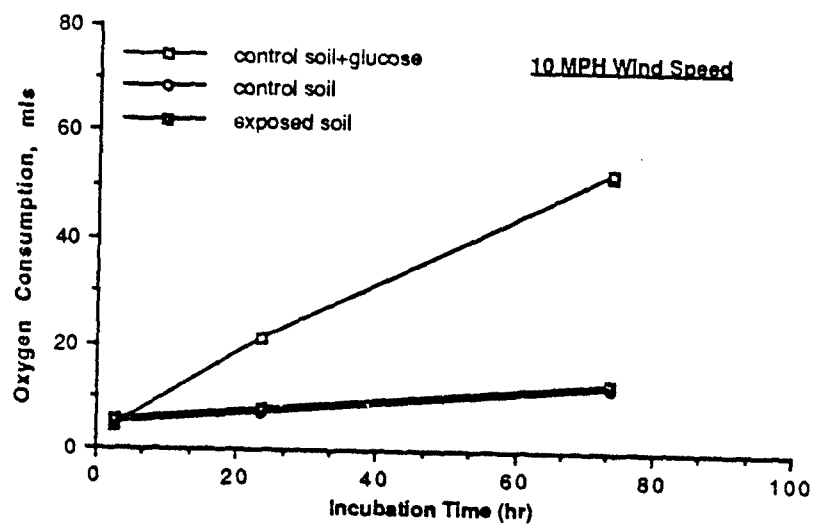


FIGURE 3.22. EFFECT OF FOG OIL EXPOSURES (10 MPH) ON PALOUSE SOIL RESPIRATION. ERROR BARS (see text) REPRESENT STANDARD DEVIATIONS, N=2.

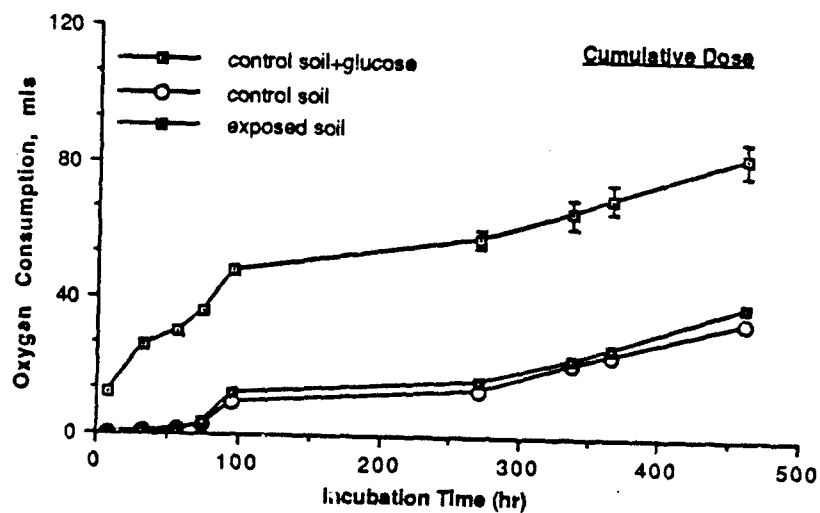


FIGURE 3.23. EFFECT OF CUMULATIVE FOG OIL EXPOSURES ON PALOUSE SOIL RESPIRATION. ERROR BARS (see text) REPRESENT STANDARD DEVIATIONS, N=2.

dehydrogenase enzyme systems catalyze the oxidation of organic material and fulfill an important role in the soil carbon cycle. The assay of soil dehydrogenase activity is a general indicator of the potential activity of the soil microbial population and has been recommended as an index of general soil microbial activity (Casida 1967; Skujins 1967).

Both stimulatory and inhibitory effects on soil dehydrogenase activity were observed when soils were exposed to fog oil at 20% to 91% relative humidity (RH) (Figure 3.24). In Burbank soil amended with glucose, dehydrogenase activity was higher (118% to 163% of unexposed control) immediately after exposure, and activity increased 2 wk later to 167% to 231% of control. Burbank soil amended with casamino acids followed the same general trend, except at 64% RH the activity was slightly inhibited in the beginning but did increase after 2 wk. In Palouse soil amended with glucose, at 20% and 64% RH, the activity was enhanced (147% to 208% of control), then decreased to the level of control soil; whereas at 91% RH exposure, the activity was inhibited initially then increased about 50%. Dehydrogenase activity in Palouse soil amended with casamino acids exhibited less stimulatory effect as compared to soil amended with glucose.

In the 10-mph wind speed smoke exposure test, smoked Burbank soil had higher dehydrogenase activity than the unexposed soil. In Palouse soil, the activity was slightly reduced (Figure 3.25).

Exposure to a cumulative dose of fog oil had a stimulatory effect on dehydrogenase activity as shown in Figure 3.26. Except for the Burbank soil amended with casamino acids, the activity was higher 2 wk after the last exposure. When soil was repeatedly exposed to fog oil smoke, it received a smaller dose of fog oil for each of the nine exposures over a period of 18 days (Table 2.5), thus the initial impact of fog oil smoke was reduced. Prolonged incubation with fog oil might adapt microorganisms to use this mixture of hydrocarbons for substrates. This may explain the distinct increase in dehydrogenase activity in soil exposed to a high cumulative dose of fog oil. The fact that exposed soil was remoistened after each exposure may have also caused the indigenous microorganisms to better utilize the increased available substrate as a carbon source.

**Soil Nitrification.** The conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and  $\text{NO}_2^-$  to  $\text{NO}_3^-$  (nitrification) in soil is a microbially mediated process important in the N cycle. Nitrate is more available for plant and microbial uptake and is more mobile in soil. *Nitrosomonas* spp. and *Nitrobacter* spp. are bacteria mediating these conversion processes. These two species are sensitive to environmental toxicants. Assaying the nitrifying bacteria in soil exposed to fog oil smoke is integral in the assessment of fog oil effects on soil microorganisms and the soil N cycle.

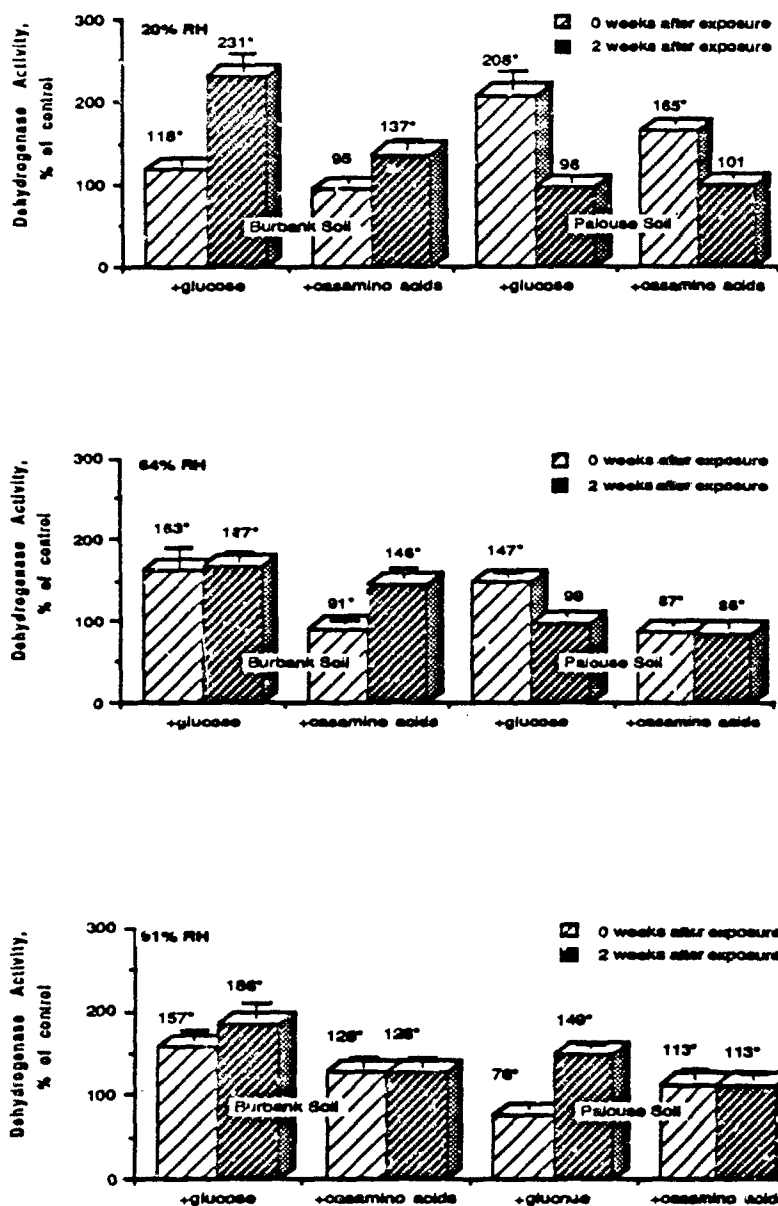


FIGURE 3.24. EFFECT OF FOG OIL ON SOIL DEHYDROGENASE ACTIVITY BASED ON RELATIVE HUMIDITY, EXPRESSED AS % OF CONTROL. ERROR BARS REPRESENT STANDARD DEVIATION,  $N=3$ . \* DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON  $t$ -TEST,  $P \leq 0.05$ .

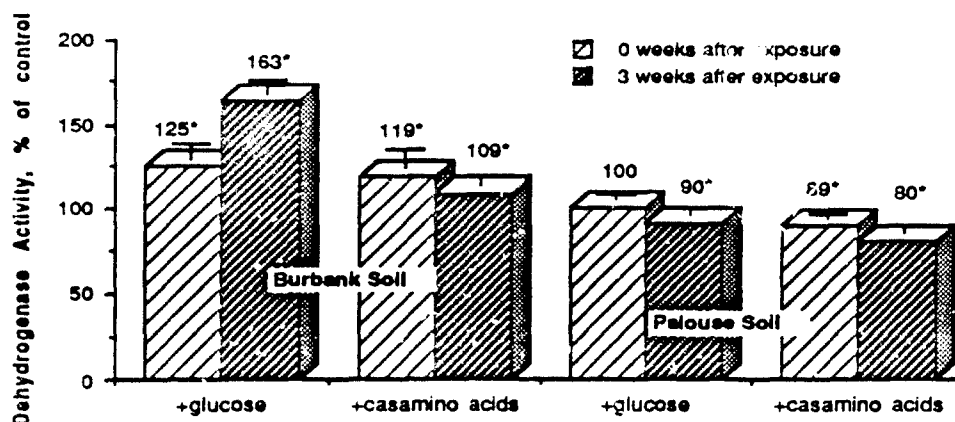


FIGURE 3.25. DEHYDROGENASE ACTIVITY (EXPRESSED AS % OF CONTROL) IN SOIL EXPOSED TO 10-MPH FOG OIL SMOKE. ERROR BARS REPRESENT STANDARD DEVIATION, N=3. \* DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON t-TEST,  $P \leq 0.05$ .

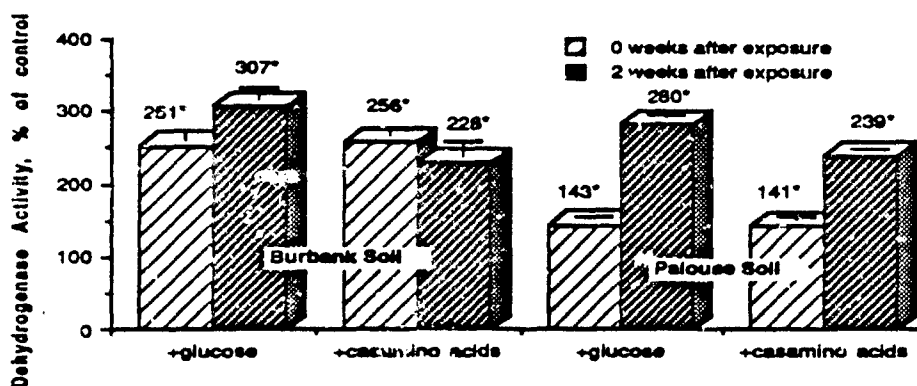


FIGURE 3.26. DEHYDROGENASE ACTIVITY (EXPRESSED AS % OF CONTROL) IN SOIL EXPOSED TO CUMULATIVE DOSES OF FOG OIL SMOKE. ERROR BARS REPRESENT STANDARD DEVIATION, N=3. \* DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON t-TEST,  $P \leq 0.05$ .



The effect of fog oil exposure on soil nitrifying bacteria was not very conclusive. Both inhibitory and stimulatory effects were observed in soils exposed to fog oil under various conditions (Figures 3.27, 3.28 and 3.29). In general, populations of nitrifying soil bacteria in both the Burbank and Palouse soils were not significantly affected by exposure to fog oil compared to populations in control (unexposed) soil even at high cumulative doses.

### 3.9 SOIL INVERTEBRATE EFFECTS

Earthworms were exposed to fog oil smokes in both the RHT and WST series. These worms were maintained in exposed in a synthetic soil mixture to provide consistency. Results are shown in Table 3.26. In each of the treatments, three replicates of six worms each were employed to evaluate mature worm mortality. In addition, each soil plate contained four unhatched cocoons to allow evaluation of hatch and survival of young individuals. The latter required that studies be conducted for 14 days to allow an average time interval for egg development. Results from both test series allowed evaluation of both RH effects and mass loading levels. In the RHT, earthworm survival was 100% except for the 91% treatment. No explanation for this deviation can be provided based on the subsequent worm data.

The extent of cocoon hatch was comparable to controls for all treatments except the rainout. Results for the WST, which involved a considerably lower dose level, showed no effect on worm mortality nor cocoon hatch.

Since fog oil appeared to have little effect on earthworm mortality, a set of in vitro assays were performed to allow evaluation of a much broader range of fog oil concentrations. The results are shown in Table 3.27. In this study, synthetic soil was amended with SGF-2 fog oil to provide a mass concentration of 0 to 571  $\mu\text{g FO/g}$  soil. This is equivalent to an aerial deposition dose of 0 to 7275  $\mu\text{g FO/cm}^2$  soil; the highest in vitro dose is approximately 10 times that for the in vivo study. The results show clearly that there is no effect of fog oil on worm mortality at concentrations below 3600  $\mu\text{g/cm}^2$ , with only nominal mortality at 3600 and 7300  $\mu\text{g/cm}^2$ . Based on the depuration studies and the latter worm studies it would appear that fog oil damage is substantially less than that for phosphorus smokes.

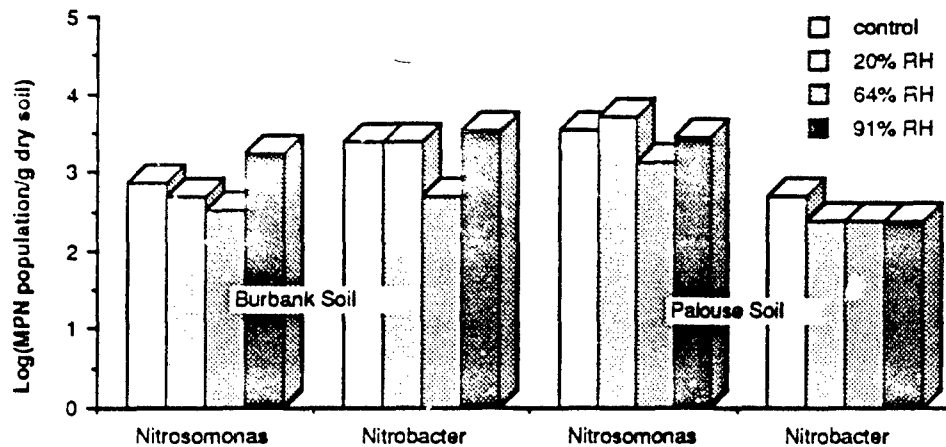


FIGURE 3.27. EFFECT OF FOG OIL ON SOIL NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE AT DIFFERENT RELATIVE HUMIDITIES. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS  $\pm 0.52$

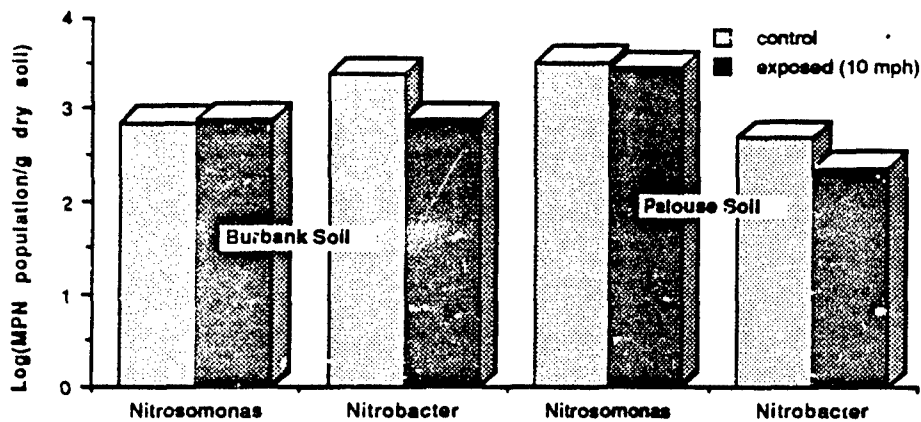


FIGURE 3.28. EFFECT OF FOG OIL SMOKE (10 MPH) ON SOIL NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS  $\pm 0.52$

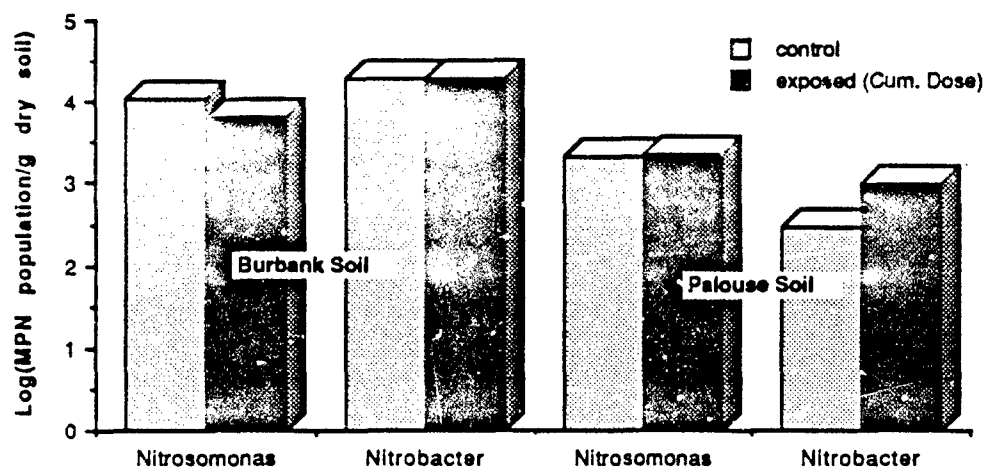


FIGURE 3.29. EFFECT OF FOG OIL SMOKE (CUMULATIVE DOSE) ON SOIL NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS  $\pm 0.52$ .

TABLE 3.26. INFLUENCE OF SOIL DEPOSITED FOG OIL ON THE SURVIVAL OF EARTHWORMS. ARTIFICIAL SOILS WITH WORMS EXPOSED TO SMOKES AND HELD FOR 14 DAYS POST-EXPOSURE.

Experiment Code	Condition	Soil Mass Loading ( $\mu\text{g FO}/\text{cm}^2$ )	Earthworm Survival	Cocoon Hatch
Control		0	18/18	8/12
FO-12	20% RH	670	16/18	8/12
FO-14	64% RH	875	18/18	9/12
FO-15	91% RH	740	8/18	9/12
FO-16	Rainout	820	18/18	5/12
Control		0	18/18	10/12
FO-17	2 mph	140	18/18	8/12
FO-19	4 mph	200	18/18	8/12
FO-20	6 mph	220	18/18	9/12
FO-18	10 mph	250	18/18	8/12

**TABLE 3.27. IN VITRO EARTHWORM ASSAY FOR SGF-2 FOG OIL AMENDED TO ARTIFICIAL SOIL, EXPOSURE DURATION 7 DAYS**

Amended Fog Oil Concentration		Earthworm Survival
( $\mu\text{g FO}/\text{cm}^2$ )	( $\mu\text{g FO}/\text{g soil}$ )	
0	0	15/15
127	10	15/15
254	20	15/15
509	40	15/15
1018	80	15/15
2037	160	15/15
3637	285	14/15
7275	571	13/15

#### 4.0 CONCLUSIONS

Environmental wind tunnels provide a method for the dynamic exposure of environmental components such as plants and soils, and subsequent elucidation of the fate and effects of obscurant smokes. This approach allows for the simulation of a number of environmental variables affecting the physical and chemical nature of smoke aerosols. In the present studies, fog oil smokes were generated at elevated temperatures and reduced oxygen to simulate nominal field generation methods, and introduced into the air stream of the recirculating tunnel, remote from the test section, to simulate aged aerosols that would be deposited 1500 m from the generator. Several environmental parameters were investigated, including exposure duration, relative humidity, wind speed, rainout during exposure and post-exposure simulated rainfall. Aerosols were continually monitored for concentration and size distribution to permit intercomparisons from test to test.

Several plant species and soil types were investigated based on dose response, intensity, and recovery. Plants were selected to be representative of native species found at regional training facilities. Investigations centered on elucidation of those physical parameters and processes affecting environmental performance resulting from recurrent use of obscurant smokes. Environmental components evaluated included foliar contact toxicity, indirect effects of soil contamination on plant growth, effects of soil-deposited smoke on soil microbial enzyme activity, and effects on earthworms. In all cases, responses were correlated with delivered dose/mass loading and not airborne smoke concentration.

Overall, results for fog oil smokes indicate a lower damage intensity than observed for phosphorus smokes resulting from foliar contact for either 8 hr or following repetitive dosing. Indirect soil/plant effects were marginal in most instances, and are not expected to be persistent. Soil microbial processes important in mineral cycling were not adversely impacted.

#### 4.1 SMOKE (AEROSOL) CHARACTERIZATION

Fog oil aerosols were generated in a controlled atmosphere wind tunnel by vaporization and condensation of SGF-2 fog oil. The aerosol was aged under simulated natural conditions and used to expose plant, soil, and other test systems. Characterization of the aerosols included primarily airborne concentration, and particle size distribution. Aerosol mass concentrations ranged from less than 100 to nearly 1000 mg/m<sup>3</sup>, depending on the test series or exposure parameter being evaluated. Particle sizes of airborne fog oil ranged from

1.6 to 3.1  $\mu\text{m}$ , and the composition of the aerosol appeared not to be affected by relative humidity over a range of 20 to 91%.

In addition to aerosol characterization, measurements of deposition to and depuration from surrogate (glass fiber filter substrate) surfaces were performed to provide a comparison with similar measurements of the experimental receptor surfaces, namely plant foliage and soil surfaces. Deposition velocities measured to surrogate surfaces (glass fiber filter coupons) exposed to a 0.9 m/s (2 mph) wind speed averaged 0.027 cm/s. Under similar conditions, average deposition velocities to plants ranged from 0.016 to 0.037 cm/s. These measurements indicated that the surrogate surfaces may approximate environmental receptor surfaces, particularly with respect to deposition velocity. However, measurements of fog oil depuration indicated that the surrogate surfaces experienced much less loss from volatilization of fog oil deposits than did plant and soil surfaces.

#### 4.2 MASS LOADING AND DEPOSITION VELOCITY TO RECEPTOR SURFACES

Values for mass loading and calculated deposition velocities to plant foliage showed significant variation between species. Plants with open canopies, such as the pines and sagebrush, were a factor of 1.5 to 2 higher than plants with closed canopies such as bush bean and fescue. The particle size and aerodynamic behavior of fog oil smoke were not affected by relative humidity, and therefore appeared to have little influence on deposition velocity and subsequent mass loading to plant or soil surfaces. Wind speed had a pronounced effect on deposition to surfaces, with deposition velocity to foliar surfaces increasing dramatically from 0.02 cm/sec at 2 mph, to 200 to 1000 cm/sec at 10 mph (Table 3.11). The differences in the rate of increase in  $V_d$  values (Figure 3.15) for closed canopy (ponderosa pine and sagebrush) versus open canopy (tall fescue) plants, may be related to the amount of turbulence encountered at the boundary between leaf surfaces and the moving air stream.

#### 4.3 RESIDENCE TIME OF FOG OIL ON SOIL AND PLANT SURFACES

Depuration of fog oil aerosol residues collected by deposition to glass fiber filter substrate under laboratory conditions was approximately 6% of the total amount deposited after 10 days and 14% after 65 days. In contrast, the depuration rate from environmental surfaces was much greater. Depuration losses from ponderosa pine were approximately 80% after 4 days, with a half-time of 1.7 days. This rather rapid loss results from volatilization from the relatively large foliar surface area. Depuration from the Maxey Flats soil was biphasic, exhibiting a rapid loss with a half-time of 20 days, followed by a reduced volatilization with a

half-time of 500 days. Depuration of fog oil from the Burbank soil was monophasic with a half-time of 58 days. Differences in behavior between soils is believed to result from both higher surface sorption in the Maxey Flats soil, which allowed for an initial increased volatilization, and a higher downward leaching in the more porous Burbank sandy loam, which reduced the initial rate of volatilization.

#### 4.4 PHYTOTOXICITY OF FOG OIL DEPOSITED TO FOLIAR SURFACES

Based on a deposited dose of 100 to 500  $\mu\text{g FO/cm}^2$ , equivalent to 2- to 8-hr exposure to smokes at 900  $\text{mg/m}^3$  air, toxicity responses are judged moderate. These are visualized as chlorosis, necrotic spotting of foliage, and leaf or needle burn. Relative humidity has no dramatic effect on the quality or intensity of damage, other than that expected based on deposited dose. Repetitive dosing at two to three day intervals resulted in substantially less damage than indicated by the total delivered dose. This amelioration in effects results from the rapid loss by volatilization of fog oil from foliar surfaces. Post-exposure simulated rainfall has little or no impact on the extent of fog oil damage. The comparatively low phytotoxicity of fog oil results from the low concentration of aromatic hydrocarbons contained in the oil. The aliphatic hydrocarbons, which are the major constituents, are less phytotoxic than aromatic hydrocarbons. However, the aliphatic hydrocarbons can affect membrane/cell permeability and likely account for the observed damage.

#### 4.5 RESIDUAL AND INDIRECT EFFECTS OF PLANT GROWTH

Residual effects, namely those that result from foliar absorption of smoke constituents transferred to below ground plant tissues, are apparent in several of the test series. While these appear to be persistent in our short term studies (2 croppings of tall fescue), the causative hydrocarbons are normally biodegradable, and the effects should attenuate in time. Indirect effects, those that impact the plant following soil deposition of smoke constituents, were somewhat dependent on soil type. In general, grass grown on Burbank soil was less affected than that grown on Maxey Flats soil. This difference may well result from the relative retention of fog oil on these two soil types. In no case was seed germination affected.

#### 4.6 SOIL MICROBIAL EFFECTS

Fog oil has little deleterious effect on soil microbial activity. On the contrary, it enhanced the microbial activities in many of the parameters assayed. Cumulative dose of fog oil exposure had no effect on soil respiration, and slightly increased the activity of nitrobacter

populations in Palouse soil, while no change was observed in Burbank soil. In addition, the cumulative dose of fog oil greatly increased soil dehydrogenase activity particularly in Palouse soil. Although exposure to fog oil at 20 to 91% relative humidity or at 10 mph wind speed showed slightly inhibitory influence in dehydrogenase activity and soil nitrifying bacteria in a few instances, respiration was not affected by these exposures. This is in contrast to exposure to red phosphorous/butyl rubber smoke, which had a strong inhibitory influence on a number of key soil microbial and enzymatic activities (Van Voris et al. 1987).

#### 4.7 SOIL INVERTEBRATE EFFECTS

Earthworm bioassays indicated no adverse effects of fog oil with exposures up to 800  $\mu\text{g}/\text{cm}^2$  soil. *In vitro* studies, where fog oil was uniformly amended to soil, showed earthworm survival to be 100% until a soil concentration of  $\sim 3600 \mu\text{g}/\text{cm}^2$  ( $285 \mu\text{g}$  fog oil/g) was reached.



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